OUTLINES OF ANALYTICAL METHODS

A guide to the occurrence, significance, sampling and analysis of chemical and microbial parameters in water

February 25 1975

TD
380
O57
1975

Ministry
of the
Environment

Ontario

The Honourable
William G. Newman,
Minister

Everett Biggs,
Deputy Minister

TD
380
O57
1975

OUTLINES OF ANALYTICAL METHODS

A guide to the occurrence, significance, sampling
and analysis of chemical and microbial parameters in water

ONTARIO MINISTRY OF THE ENVIRONMENT

LABORATORY SERVICES BRANCH

FEBRUARY 25, 1975

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

FOREWORD

Information on analytical methods is often required in order to correctly interpret data and to prepare reports. This collection of analytical outlines has been assembled in order to provide pertinent information in a brief non-technical form and to assist the sampler in understanding the meaning behind certain chemical and microbial parameters as well as their limitations. The outlines are not intended to be guides for performing the analysis.

Methods in this manual are suitable for routine chemical and microbiological analyses on water samples and include specific instructions as to proper sampling and preservation techniques. Some non-routine methods are described in the appendices. Information regarding other tests can be obtained by contacting the Laboratory Services Branch, Ontario Ministry of the Environment.

Individual test descriptions will be revised periodically as needed. Samplers are urged to fill out the appropriate form at the back of this manual so that they can be notified as quickly as possible whenever changes take place.

INTRODUCTION

The various laboratories of the Laboratory Services Branch are equipped to perform a large number of standard chemical and microbial analyses on domestic water supplies, surface waters, ground waters, domestic wastes and industrial wastes. Special analyses, required for research studies and unusual pollution problems, can also be provided. Some of these are mentioned in the appendices.

The decentralization of the Ontario Ministry of the Environment has progressed to the stage where three regional laboratories are operational in addition to the main Toronto laboratory. The boundaries of the districts serviced by these laboratories are illustrated in the figure on the next page. Samples collected in Regions 2,3 and 5 are analyzed in Toronto. Samples collected in Regions 1,4 or 6 are analyzed in London, Kingston or Thunder Bay respectively. The tests performed by each Regional Laboratory as well as the four sectional laboratories in Toronto are shown in Table I. Notice that a number of parameters are only handled in Toronto. Samplers should check to see which parameters are analyzed at which laboratories so they do not ship their samples to a laboratory which is incapable of providing the requested analyses. For major surveys and studies in areas remote from the regular laboratories, mobile laboratories and field stations are often provided.

CHEMICAL TESTING

Collection and Perishability of Samples

The method of collecting the sample in the field is the concern of the individual in charge of the particular survey. If the sample is not representative of the whole, the subsequent analyses will be worthless. Care must be taken to prevent contamination of the sample by sampling devices, motor exhausts, disturbing the sediment beds of lakes etc. Furthermore, it must be realized that the composition of most samples will change with time; thus the sample must be quickly forwarded to the laboratory for analyses. The perishability of a sample may be due to biological activity, chemical precipitation, leaching of contamination from containers, adsorption on the walls of containers, chemical reactions between constituents, and volatility. Tests such as dissolved oxygen, dissolved carbon dioxide, free chlorine, and pH are examples of extremely perishable parameters; field analyses are recommended whenever possible.

In view of the probable chemical degradation of a sample, the laboratory analyzes each sample as rapidly as present facilities permit. The average number of tests possible per day is included in each method outline; this number could only be increased by reassigning staff deducted from other analytical functions. This number provides a guideline which will allow samplers to regulate their sample inputs and avoid pre-empting a large portion of the daily capacity for any given test. Your co-operation will assist the laboratories in maintaining a quick and efficient analytical service.

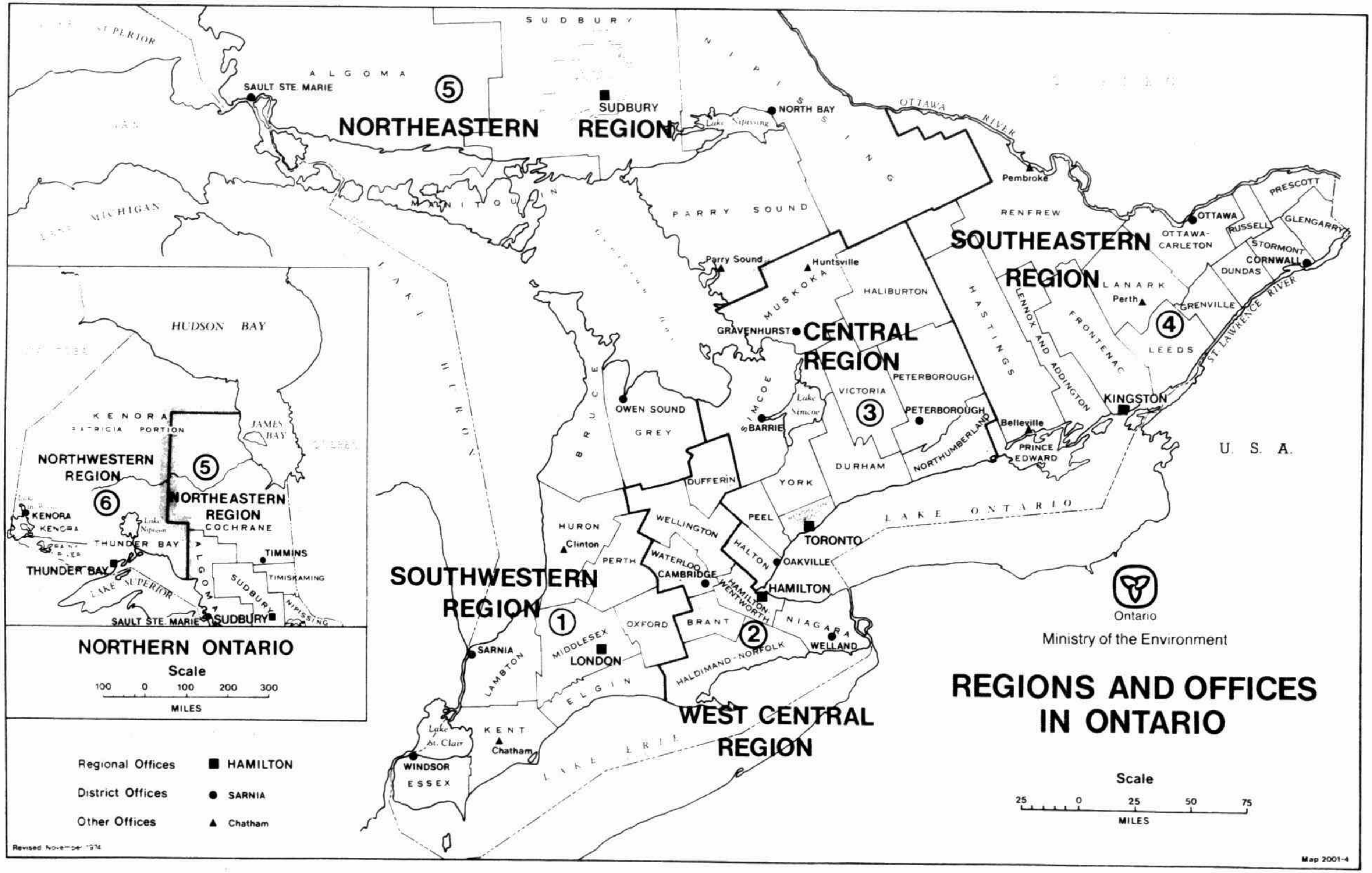
REGIONS AND OFFICES IN ONTARIO

TABLE I

ANALYTICAL TESTING CAPABILITIES

PARAMETER	TORONTO RIVERS & LAKES	TORONTO PROCESSED WATER	TORONTO I.T.C.	TORONTO O.T.C.	LONDON	THUNDER BAY	KINGSTON
ACIDITY	X	X			X	X	X
ALKALINITY	X	X			X	X	X
ALUMINUM			X				
AMMONIA NITROGEN	X	X			X	X	X
ANIONIC DETERGENTS (MBAS)		X			X	X	
ARSENIC			X			X[1]	
BARIUM			X				
BIOCHEMICAL OXYGEN DEMAND	X	X			X	X	X
BORON			X				
CADMIUM			X			X	
CALCIUM	X	X	X		X	X	X
CARBON	X						
CARBON DIOXIDE	X	X					X
CHEMICAL OXYGEN DEMAND	X	X			X	X	X
CHLORIDE	X	X			X	X	X
CHLOROPHYLL	X					X	
CHROMIUM			X				
COBALT			X			X	
COLOR-APPARENT	X	X			X	X	X
CONDUCTIVITY	X	X			X	X	X
COPPER			X			X	
CYANIDE			X				
FLUORIDE		X			X		
HARDNESS	X	X			X	X	X
IRON (TOTAL)	X		X		X	X	X
LEAD			X			X	
LITHIUM			X				
MAGNESIUM	X	X	X		X	X	X
MANGANESE			X			X[1]	
MERCURY			X			X[1]	
MOLYBDENUM			X				
NICKEL			X			X	
NITRATE NITROGEN	X	X			X	X	X[2]
NITRILOTRIACETIC ACID				X			
NITRITE NITROGEN	X	X			X		X[2]
NITROGEN-TOTAL KJELDAHL	X	X			X	X	X
ORTHOPHOSPHATE - FILTERED REACTIVE	X	X			X	X	X
PESTICIDES				X			
PETROLEUM HYDROCARBONS				X			
pH	X	X			X	X	X
PHENOLICS (REACTIVE)	X			X	X	X	
PHOSPHORUS - TOTAL	X	X			X	X	X
POTASSIUM	X	X			X	X	X
RESIN & FATTY ACIDS				X			
SELENIUM			X				
SETTLEABILITY		X					
SILICATES-REACTIVE	X				X		
SILVER			X				
SLUDGE VOLUME INDEX		X					
SODIUM	X	X			X	X	X
SOLIDS-DISSOLVED	X	X			X	X	X
SOLIDS-IGNITED	X	X			X	X	X
SOLIDS-SUSPENDED	X	X			X	X	X
SOLVENT EXTRACTABLES				X			

TABLE I (Contd)

PARAMETER	TORONTO RIVERS & LAKES	TORONTO PROCESSED WATER	TORONTO I.T.C.	TORONTO O.T.C.	LONDON	THUNDER BAY	KINGSTON
STRONTIUM				X			
SULFATE	X	X			X	X	X
SULFIDE			X		X		
TANNINS & LIGNINS				X			
TITANIUM			X				
TURBIDITY	X	X			X	X	X
URANIUM			X				
VANADIUM			X				
VINYL CHLORIDE (MONOMERIC)				X			
VOLATILE ACIDS		X			X	X	
ZINC			X			X	

[1] TEST WILL BE AVAILABLE IN THE NEAR FUTURE

[2] TOTAL NITRATE PLUS NITRITE REPORTED AS NITROGEN

Specific sampling information is provided in each method outline. If there are any questions, the sampler should consult with laboratory staff before the samples are collected.

Sample Containers and Preservation Techniques

In general, water samples are collected in 32 oz. glass bottles, but some analyses require plastic containers. Many procedures call for sample preservation. Table II includes a summary of both the preferred container type as well as the preservation techniques for each parameter, while the individual outlines provide more detail. Remember that some parameters are stabilized by a certain preservation technique while others are completely altered or destroyed. Be sure that the preservation technique is consistent with the tests requested.

Sludge samples should be collected in wide mouth glass bottles and never filled more than half way. If they are filled too full, the production of gaseous compounds may cause the containers to explode while in transit or at the laboratory.

Special acid washed plastic containers are required for trace level heavy metal determinations on domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples. With the exception of mercury, samples for heavy metal analyses are preserved by adding 1 ml of concentrated nitric acid (20 drops) to one litre of sample after the sample is in the container. Never add acid to an empty plastic container prior to sampling. Strong acid will activate plastic surfaces in such a way that some heavy metals may be adsorbed onto the container walls. The use of foil lined caps should be avoided when sampling for trace quantities of heavy metals.

Sample Volumes

Each method outline specifies the volume of sample required for proper analysis on all sample types. For the great majority of tests, however, the volume needed depends on sample strength with "weaker" or clean samples (e.g. domestic water supplies, well waters, and unpolluted surface waters) requiring the largest volumes. For a sample containing low concentrations of a substance, the largest practical volume is tested in order to provide a sufficient quantity of that substance for reliable detection. For "stronger" samples (effluents and sewages), a smaller amount or even a dilution may be employed.

In many instances samplers do not provide a sufficient quantity of sample to complete all the requested analyses. This is extremely frustrating to both the sampler who finds half of his analyses marked "SAMPLE EXHAUSTED", as well as the laboratory technician who spends 15 minutes of his time hunting down an empty bottle. If the sampler feels that the available volume of sample is insufficient for all his requested analyses and if it is impossible to acquire more sample, consultation with laboratory staff is recommended. This will enable the laboratory to assess his requirements and make the best use of the available sample.

Samplers are asked to submit at least 6 ounces of sample in excess of their original estimate. If the volume chosen for a test proves inappropriate to the strength of the sample, the test can be repeated. In addition, following completion of all tests, the results are reviewed to detect any calculation errors, uncertainty as to the composition, etc. It is of great assistance to have sufficient sample left to provide visual confirmation of its quality in comparison with the results obtained.

The best way to estimate the total required volume of sample is to sum the specified individual volumes for each test plus the extra 6 ounces discussed above. A number of tests, however, may be determined simultaneously on the same aliquot; therefore samplers should consider the following criteria before deciding on a total volume.

1) Both total phosphorus and Kjeldahl-nitrogen can be determined on a single 75 ml (3 ounce) aliquot.

2) Nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen (free ammonia) and filtered reactive orthophosphate can all be determined on a single 75 ml (3 ounce) aliquot.

3) Both sodium and potassium can be determined on a single 40 ml (2 ounce) aliquot.

4) Aluminum, copper, cadmium, cobalt, chromium, iron, lithium, molybdenum, manganese, nickel, silver, strontium, and zinc can all be determined on a single 400 ml (14 ounce) aliquot. For very low levels, preconcentration necessitates that one full container (900 mls) be submitted for metals. In the latter case samples must be clearly labelled "For Preconcentration."

Information to be Provided on Sample Submission Forms

The required analytical parameters should be listed on the back of the Sample Submission Form. Samples cannot be accepted with such requests as "Chemical analysis" or "All the metals." Even a request for "Pesticide analysis" is unsatisfactory as there are hundreds of formulations in use to-day; if the sampler cannot identify the particular pesticide, he should specify the chemical class e.g. chlorinated hydrocarbons, carbamates, 2,4 D herbicides, organophosphates, etc. (See Appendix I). If there is doubt concerning which analyses to request, a brief description of the general problem or reason for sampling will enable the laboratory staff to select the appropriate tests. Samplers should always provide their telephone number or the telephone number of someone responsible for their samples. This will facilitate sample processing in case any uncertainties arise regarding the instructions on the submission forms.

If a group of related samples is submitted, a map of the area or the relative location of waste inputs is very helpful to the laboratory staff. Please number the samples in a logical order, e.g. downstream in a river. All analyses are routinely screened for anomalous results before they are released. Suspicious results might be improperly rejected whereas some details as to the location would confirm their validity.

When a sample is sent to the laboratory a description of known constituents should be included on the submission sheet, particularly an unusual one such as an industrial waste contaminant. Interferences (reactions which produce false analytical results) can be eliminated by pretreatment if the analyst is forewarned. Samples known to contain cyanide, arsenic, mercury or other toxic materials should be clearly marked for the protection of laboratory personnel.

Identification of unknown contaminants is very time consuming. Samples should be as large as possible to allow a wide range of exploratory tests. The sampler should indicate whether qualitative or quantitative results are required. Any available information concerning the sampling point, possible contaminants, and industries implicated is extremely important for such samples.

Samples which are not homogeneous present analytical difficulties because it is virtually impossible to take a representative aliquot. If the sampler is only interested in one phase (aqueous, solid or immiscible organic), he should label the submission form accordingly. Otherwise the laboratory will consider the whole sample, and take aliquots of the mixture.

Samples sent to Toronto could be analysed by as many as four different laboratories; the distribution of analyses among these sections is shown in Table I. Sample processing is much more efficient if the sampler submits separate forms and separate sample containers if testing is to take place in more than one of these sectional laboratories. Your co-operation in this respect will be truly appreciated by everyone involved.

Analytical Repeatability and Accuracy

The correctness of a result produced by laboratory staff is limited by many factors, which include the care taken in sampling, the stability of the sample, sample handling and preservation, and analytical variability.

The repeatability of the analysis is measured in units of standard deviation, determined by analyzing the same sample several times. Each result will be slightly different, but they will all tend to fall within a narrow range of values centered on their average. Under certain circumstances, it can be assumed that the next replicate result will also fall within this range and, in fact, fewer than 5% of the replicates are expected to fall outside of ± two standard deviations on either side of the average value (fewer than 1% are expected to fall outside of ± three standard deviations). If only one analysis is performed, there is no way to tell whether it is one of the 5 in 100 results outside of ± two standard deviations, but over the long term there is a 2 out of 3 chance that it is within ± one standard deviation of the average value.

Note that repeatability (i.e. the standard deviation) is a function of the technique used under routine conditions of operation. If better performance is required by the data user, he should communicate with the appropriate analyst to determine if this is possible within the operational constraints of the laboratory.

Unfortunately, repeatability does not in itself guarantee that the individual (or average) result is "on target". Different analysts tend to introduce their own bias which may change from day to day. Control measures are routinely employed at the various laboratories to ensure data quality, but sampling, sample handling and perishability may all have a significant effect on the accuracy of the results. Both sampler and analyst must work together to ensure that the best quality data is provided for the task at hand.

MICROBIOLOGICAL TESTING

COLLECTION OF SAMPLES

Sterile sampling bottles are available through Central Stores in Toronto. For special studies, alternate bottles are obtainable directly from the Microbiology Section on consultation. It is the responsibility of the sampler to use aseptic techniques when handling these sterile bottles. Meaningless results are obtained when contamination occurs through faulty handling of sterile containers.

SURFACE SAMPLES

Clamp the bottle onto a sampling pole before removing the cap. Touch only the outer surface of the cap when opening the bottle. The inner lip and liner must not come in contact with anything except the atmosphere. If the inner surfaces of the cap or bottle lip are accidentally touched, the sample has been contaminated and should not be submitted. It is recommended procedure to hold the cap with your fingertips until the sample has been taken. The cap must not be set down somewhere while the sample is being taken as this will result in contamination.

Surface sampling is accomplished by quickly lowering the sample bottle into the water approximately one meter below the surface with the mouth facing into the current. When sampling near shore, care should be taken to get a sample uncontaminated with sediment. The bottle is then removed from the water, the level adjusted to the top of the label, immediately capped, and then unclamped from the sampling pole. Samples must be collected using this prescribed technique. The use of a dipper or other sampling device will result in contamination.

DEPTH SAMPLES

Depth samples are taken using sterile sampling bulbs which can be obtained from the Microbiology Section in Toronto. Bulbs should be used as quickly as possible: if not used, they should be returned to the Microbiology section within a maximum of two weeks otherwise the rubber will crack and the bulb will not open. The same care that is used with sampling bottles must be used in the handling of bulbs. The glass plugs supplied have been sterilized within a cellophane envelope and must not come in contact with any contaminated surfaces when they are being removed from the cellophane envelope. If, for some reason, the sampler should run out of glass rods, he may dip the metal plug into alcohol and flame it. After flaming, the plug is immediately inserted into the bulb, taking the usual precautions when handling sterile equipment. The use of the metal plug is discouraged and it should only be used in rare instances when the sample could not possibly be obtained at a later time in the correct manner.

TAP SAMPLES

Prior to sampling from a tap, the water should be allowed to run at full flow for approximately two minutes. The strong flow will clean out residual contamination around the orfice of the tap thus providing for a more representative sample. The water pressure may then be reduced to permit taking the sample without excessive splashing which could result in contamination of the sample.

Fill the bottle to the top of the label being certain that the mouth of the bottle does not come in contact with the tap or any contaminated surface. The cap must also be handled aseptically as described previously.

PERISHABILITY OF SAMPLE

With time samples undergo changes (increases or decreases) in bacterial population, depending upon the initial bacterial density, the presence of growth-promoting or toxic substances in the water and the environmental conditions under which the samples are held during transport to the laboratory. Analyses should be performed as soon as possible after collection, preferably within six hours, but not exceeding 24 hours.

Drinking water samples received 24 to 48 hours after collection may be analyzed, but the results are not normally interpreted because of changes in the bacterial population. Samples received after three days are rejected. Negative coliform results for drinking water samples arriving more than 48 hours after collection should be considered incorrect and fresh samples should be collected.

SAMPLE CONTAINERS AND PRESERVATION TECHNIQUES

Pre-sterilized 6-ounce bottles with blue labels are usually adequate for the routine sampling of water from distribution systems, surface waters, well waters etc. provided the waters have not been chlorinated. Chlorinated waters must be sampled in pre-sterilized 6-ounce bottles containing sodium thiosulfate as a preservative (red label). Sodium thiosulphate will neutralize the disinfecting capabilities of the chlorine thereby preserving the existing microbial population at the time of sampling. Samples collected for special "nuisance" organism analyses should be collected in regular (blue label) sample bottles.

Samplers should check to see if the plastic seal on each container is intact before sampling. Containers with seals which are loose or cracked should not be used.

All samples should be collected early in the week and shipped to the appropriate laboratory without delay. During the Spring, Summer and Fall, samples must be packed in ice in order to minimize biological activity. During the Winter, samples should be placed in an insulated container that will prevent freezing while still keeping them cold.

SAMPLE VOLUMES

In general, one bottle or bulb per sample provides sufficient volume for standard analysis. If, however, the bacterial levels expected are very low or extra parameters are being requested, then additional samples may be required. Consultation with the Microbiology Section is advisable in such cases. When a duplicate sample is being taken, it should be obtained at the same time as the first sample. This can be achieved for surface samples by clamping two bottles on a sampling pole and for depth samples by placing two bulb samplers on the sampling line in a 'piggy-back' fashion.

ROUTINE BACTERIOLOGICAL ASSESSMENT

One of the prime reasons for inclusion of bacteriological parameters in water quality assessment is to indicate the presence of fecal contamination and thus the possible presence of pathogenic bacteria. Since the determination of specific pathogens in water is generally slow, laborious and uneconomical, specific groups of bacteria are generally used as indicators of fecal contamination. The standard groups of micro-organisms are:

1) Total Coliforms (TC). This group of bacteria comprises species that are commonly associated with fecal matter (human and animal) and normal inhabitants of soil and vegetation.

2) Fecal Coliforms (FC). These bacteria are mainly species associated with human and animal fecal matter and indicate a relatively recent pollution input.

3) Fecal Streptococci (FS). This group of bacteria is largely associated with fecal pollution from animals and to a lesser extent man. The geometric mean of the FS and FC results may be used to gain information on the source (human or non-human) of pollution within areas adjacent to or at an input.

Other specialized bacteriological parameters that provide information on general water quality and industrial pollution are available upon consultation with the Microbiology Section.

Sampling

Minimum Volume of Sample	Required Sample Container	Special Handling Technique
150 mls (6 ounces)	Pre-sterilized glass bottles or rubber syringes	Pack in ice immediately after sampling. Use bottles containing thiosulfate for chlorinated water

TC, FC and FS levels will undergo change even upon refrigeration; therefore, immediate delivery to the laboratory is essential. Analyses should be performed as soon as possible after collection, preferably within six hours, but not exceeding 24 hours. The necessary frequency of sampling is outlined in the M.O.E. Guidelines and Criteria booklet (15).

Method

Analysis for all three parameters is by membrane filtration (MF) according to Standard Methods (1) using M-Endo Agar LES (Difco) for TC, MacConkey Membrane broth (Oxoid) for FC and M-Enterococcus Agar (Difco) for FS. All results are reported as counts/100 ml.

Drinking water samples are normally examined by the presence-absence (P-A) procedure for TC, FC and FS as well as the MF procedure for TC.

Time of Analysis

The number of analyses performed per day will depend on the type of sample, the number of dilution steps required, the number of parameters requested and the incubation periods for each parameter.

SHIPPING PROCEDURES

CN Express and CP Express provide the fastest and most reliable service for the shipment of environmental water samples in Ontario. Air Express, parcel post, bus companies and other services discourage the shipment of water samples because of the damage caused to other shipments when breakage occurs.

Contract numbers are important as they provide the only means for tracing a lost shipment. Every shipment is assigned a contract number at the Express Depot, but it is generally up to the sampler to attach this contract number to each carton of his shipment. Identification stickers are provided by the Express companies upon request. Samplers are urged to keep a record of all their contract numbers.

The following addresses should be used when shipping samples to the various laboratories.

1) Central Region - Main Toronto Laboratory

Ontario Ministry of the Environment,
Central Stores,
Resources Road,
Highway 401 and Islington,
Toronto, Ontario

2) Southwestern Region - London Laboratory

Ontario Ministry of the Environment,
Southwestern Regional Laboratory,
985 Adelaide St. S.
London, Ontario.

3) Northwestern Region - Thunder Bay Laboratory

Ontario Ministry of the Environment,
Thunder Bay Regional Laboratory,
411 Donald St. E.,
Thunder Bay, "F", Ontario.

4) Southeastern Region - Kingston Laboratory

Ontario Ministry of the Environment,
Southeastern Regional Laboratory,
133 Dalton St.,
Kingston, Ontario.

Requisition for new containers need only include the pack numbers and stock numbers listed below.

SPECIAL PACKS

STOCK NUMBER	PACK NUMBER	CONTENTS	WEIGHT	COST
70 P 21	Pack # 1	8 - 32 oz. Glass	12 lbs.	$3.00
70 P 22	Pack # 2	2 - 32 oz. Glass	3 lbs.	.70
70 P 23	Pack # 3	1 - 32 oz. Glass	2 lbs.	.45
70 P 24	Pack # 4	8 - 32 oz. Glass W.M.	15 lbs.	5.50
70 P 25	Pack # 5	16 - 16 oz. Glass W.M.	15 lbs.	6.50
70 P 26B	Pack # 6B	2 - 6 oz. Bacti Blue	1 lb.	.50
70 P 26T	Pack # 6T	2 - 6 oz. Thio Red	1 lb.	.50
70 P 26P	Pack # 6P	2 - 6 oz. Phenol Green	1 lb.	.50
70 P 27B	Pack # 7B	4 - 6 oz. Bacti Blue	2 lbs.	.90
70 P 27T	Pack # 7T	4 - 6 oz. Thio Red	2 lbs.	.90
70 P 27P	Pack # 7P	4 - 6 oz. Phenol Green	2 lbs.	.90
70 P 28B	Pack # 8B	72 - 6 oz. Bacti Blue	40 lbs.	16.50
70 P 28T	Pack # 8T	72 - 6 oz. Thio Red	40 lbs.	16.50

Further enquiries regarding container requisitions, shipping procedures, etc. should be directed to Central Stores in Toronto (telephone 248-3020).

SAMPLE ENQUIRIES

All samples received by the Laboratory Branch are assigned numerical codes according to sample type. When the analyses are completed, the results are entered onto the original submission sheets, checked by the scientist-in-charge, and sent for typing. All original submission sheets are retained in the sample reception files. Laboratory staff are prepared to answer questions regarding the receipt and progress of samples but require the following information:

1) Municipality or Township in which the sample source is located.

2) Name of engineer, biologist, etc. to whom the analytical report is to be submitted.

3) Name of program or study.

4) Sampling date and estimated day of arrival at the laboratory.

5) Location codes or other sample identification number. Laboratory numbers are preferred, if known.

6) Type of sample (e.g. water, river, sewage, industrial wastes, Great Lakes, etc.).

The following is a listing of telephone numbers where enquiries are handled most frequently:

Microbiology Section

Water Quality	A. Burger (Supervisor)	248-3008
Rivers and Lakes	J. Clark (Supervisor)	248-3008
Process Wastes	F. Thompson (Scientist)	248-3008
Water Quality Lab.	S. Debreceni	248-3008
Great Lakes	M. Young (Scientist)	248-3008

Water Quality Section

Process Monitoring	B. Stundzia (Supervisor)	248-3064
Process Monitoring	J. Crowther (Control Chemist)	248-3064
Domestic Water Analyses	M. Rawlings	248-3024
Domestic Waste Analyses	B. Cheung	248-3022
Rivers and Lakes	J. Adamski (Control Chemist)	248-3064
Rivers and Lakes - Eutrophication Parameters	P. Millar	248-3054
Rivers and Lakes - Mineral Analyses	S. Wisz	248-3026

Organic Trace Contaminants Section

Pesticides (Insecticides, Herbicides and related Micropollutants)	G. Rees (Supervisor)	248-3743
	J. Osborne	248-3743
Spectroscopy (Bunker Fuel Oil spills and routine organics)	G. Wyhovszky (Supervisor)	248-3469
Chromatography (Gasoline spills, Oil spills and special organics)	Dr. A. Nicholson (Supervisor)	248-3913
	B. Gutteridge	248-3913
Mass Spectrometry (Identifications and special organics)	W. Duholke	248-3913

Inorganic Trace Contaminant Section

Effluents	Dr. B. Loescher	248-3775
Sediments and soils	F. Darcel	248-3775
Spectrography	Dr. M. Moselhy	248-3029
Organometallics	Dr. O. W. Berg	248-3775

London Regional Laboratory

D. Glutek (Chief)	681-3600
Dr. W. Cook	681-3600
G. Palmateer	681-3600

Thunder Bay Regional Laboratory

A. Perras (Chief)	622-5851
M. Mazurski	622-5851
G. Irwin	622-5851

Kingston Regional Laboratory

S. MacBeth (Chief)	549-4000

ANALYTICAL OUTLINES

Each chemical test performed by the various laboratories is described in the following single page outlines which are listed alphabetically according to the assigned test titles in Table II. Each outline contains a variety of information which can be used by the samplers in choosing the most applicable parameters for a particular problem or situation and in interpreting their data.

The following definitions are provided to familiarize the sampler with the analytical specifications provided in this manual. A proper understanding of these definitions would help minimize the improper use of chemical data.

RANGE OF APPLICATION

The range of application described in each method has been chosen to accommodate the majority of samples in a routine manner. It is not necessarily a definitive limitation on an analytical technique. Samplers should consult with laboratory staff regarding individual requirements since in some cases, the specified range may be extended to lower or higher levels.

DETECTION LIMIT

The detection limit is the value below which one is unable to confirm a positive response for a particular chemical parameter. No chemical method is ever sensitive enough to confirm that nothing is there. Samplers are urged to be extra cautious in interpreting data which is very close to the defined detection limit, since analytical variability becomes large relative to the amount being measured.

PRECISION

Precision is a measurement which defines the inherent variability associated with a particular analytical method. When used in the context of this manual, precision refers to the "standard deviation" amongst multiple analyses on a single sample. The interpretive value of analytical data is greatly dependent upon precision since it is the fundamental criteria for distinguishing between real changes in water chemistry and analytical variability.

The precision of a method will vary somewhat over its routine operating range. Therefore, the precision is most correct when reported at a particular concentration level. In the context of this manual, most of the reported precisions apply to the bottom half of the operating range unless a particular level is specified. As a rough rule of thumb, the precision at the bottom end of an operational range should be doubled for levels in the middle of the range and quadrupled for levels at the top end of the range.

SIGNIFICANT FIGURES

It is frequently the custom of analysts to round off their data before reporting results to avoid implying that the precision of their analytical technique in any way reflects the reliability of the result as it relates to the actual environmental conditions from which the sample was taken. In most cases the data is reported to two significant figures, but, as will be shown below, this can cause the data user to over or under-estimate the quality of the data.

The number of significant figures is based on the number of digits reported excluding decimal positioning zeros. Thus .00541,.541 and 541. all contain three significant figures. The number 541000. is ambiguous, depending on how many of the zeros are for decimal positioning, and is best reported as 5.41×10^5 if three figures are significant or as 5.410×10^5 if four are significant.

Since the last significant figure can be expected to vary by at least ±1, an estimate of the implied maximum reliability can be made (eg ±1 in 541 is approximately ± 0.2%) as in the following table. (The decimal positioning can be adjusted to suit other ranges of numbers).

	Data reported in the range	Significant figures	Implied reliability	Quality of data
a)	0.01 - 0.09	1	100 - 10%	very poor
b)	0.10 - 0.19	2	10 - 5%	poor
c)	0.20 - 0.99	2	5 - 1%	good
d)	1.00 - 1.99	3	1 - .5%	excellent
e)	2.00 - 9.99	3	< .5%	see below

The better analyst will attempt to report data to within a reproducibility of ±5% provided that

a) the detection limit of his analytical system permits this

b) the range of routine samples received in his laboratory permit the use of the best detection limit available

c) the economics under which he operates permit him to set up two or more operating ranges if necessary

d) the samples as received can be aliquoted in a representative fashion to within 5%

Under these conditions, continuing the example in the above table, he would attempt to report to the nearest 0.005 in the range 0.10 to 0.19 and would probably round-off data to the nearest 0.05 in the range 1.0 to 1.9 units. Results from replicate samplings strongly suggest for a variety of reasons that the practice of reporting three significant figures as in e) above cannot be justified except to more clearly define the second figure. Note that, as the concentration approaches the detection limit, for the dilution and the methodology being applied, the relative reproducibility approaches

± 100%. The presence of only one significant figure in the reported result indicates a result near the detection limit of an operational range. Under these conditions, if the dilution factor chosen was larger than that routinely applied, the test will usually be repeated so as to provide two significant figures.

SUMMARY

The operating range, detection limit, and precision for a particular parameter greatly depends on the type of samples being analyzed. Open water samples (e.g. unpolluted rivers and lakes) can be analyzed to lower detection limits and better precision than Domestic and Industrial Waste samples. Specifications for all standardized operational ranges are presented in Table II.

TABLE II A

CHEMICAL PARAMETER	PREFERRED SAMPLING CONTAINER	PRESERVATION TECHNIQUE	MINIMUM VOLUME OF SAMPLE (mls)	ANALYTICAL TECHNIQUE
ACIDITY	GLASS OR PLASTIC	None*	50	Manual NaOH titration
ALKALINITY	GLASS OR PLASTIC	None*	50	Fisher Titralyzer; Radiometer A.T.S.
ALUMINUM	PLASTIC & GLASS*	HNO$_3$ (20 Drops/Bottle)	100	A.A.S.†
AMMONIA NITROGEN (FILTERED)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE	75	Technicon Auto Analyzer
ANIONIC DETERGENTS (MBAS)	GLASS	REFRIGERATE	100	Chloroform Extraction and Colorimetry
APPARENT COLOR	- SEE COLOR-APPARENT			
ARSENIC	PLASTIC OR GLASS	NONE	50	Flameless A.A.S.†; Colorimetry
BARIUM	PLASTIC & GLASS*	HNO$_3$ (20 Drops/Bottle)	100	A.A.S.†
BIOCHEMICAL OXYGEN DEMAND	GLASS	REFRIGERATE	500	Dissolved Oxygen Membrane Probe
BOD$_5$	- SEE BIOCHEMICAL OXYGEN DEMAND			
BORON	PLASTIC ONLY	NONE	100	Manual Colorimetry
CADMIUM	PLASTIC & GLASS*	HNO$_3$ (20 Drops/Bottle)	100	A.A.S.†
CALCIUM	GLASS OR PLASTIC	NONE	100	Manual EDTA Titration; A.A.S.†
CARBON	GLASS OR PLASTIC	REFRIGERATE	50	Beckman Infrared Analyzer
CARBON DIOXIDE	SPECIAL*	REFRIGERATE	*	Manual NaOH Titration
CHEMICAL OXYGEN DEMAND	GLASS	REFRIGERATE	25	Manual Reflux and Redox Titration
CHLORIDE	GLASS	NONE	50	Radiometer ATS; Fisher Titralyzer Technicon Auto Analyzer
CHLORINATED HYDROCARBON	- SEE PESTICIDES			
CHLOROPHYLL	FIELD FILTRATION*	10% MgCO$_3$ (1 ml/l)	1000	Colorimetry According to UNESCO (16)
CHROMIUM	PLASTIC & GLASS*	HNO$_3$ (20 Drops/Bottle)		A.A.S.†; Colorimetry
COBALT	PLASTIC & GLASS	HNO$_3$ (20 Drops/Bottle)	100	A.A.S.†
COD	- SEE CHEMICAL OXYGEN DEMAND			
COLOR - APPARENT	GLASS	REFRIGERATE	75	Lovibond Nesslerizer
CONDUCTIVITY	GLASS OR PLASTIC	NONE*	75	Radiometer CDM3
COPPER	PLASTIC & GLASS*	HNO$_3$ (20 Drops/Bottle)	100	A.A.S.†
CYANIDE	GLASS OR PLASTIC	50% NaOH (1 ml/bottle)*	500	Manual AgNO$_3$ Titration; Colorimetry
DETERGENTS	- SEE ANIONIC DETERGENTS (MBAS)			
DISSOLVED SOLIDS	- SEE SOLIDS - DISSOLVED			
ETHER SOLUBLES	- SEE SOLVENT EXTRACTABLES			
FATTY ACIDS	- SEE RESIN AND FATTY ACIDS			
FILTERED REACTIVE ORTHOPHOSPHATES	- SEE ORTHOPHOSPHATES - FILTERED REACTIVE			
FLUORIDE	GLASS OR PLASTIC	NONE	50	Technicon Auto Analyzer; Ion Specific Electrode
FREE AMMONIA	- SEE AMMONIA NITROGEN			
HARDNESS	GLASS OR PLASTIC	NONE*	50	Manual EDTA Titration
HEXAVALENT CHROMIUM	- SEE CHROMIUM			
HYDROCARBONS	- SEE PETROLEUM HYDROCARBONS AND PESTICIDES			
IGNITED SOLIDS	- SEE SOLIDS - IGNITED			

CHEMICAL PARAMETER	PREFERRED SAMPLING CONTAINER	PRESERVATION TECHNIQUE	MINIMUM VOLUME OF SAMPLE (mls)	ANALYTICAL TECHNIQUE
IRON (TOTAL)	GLASS OR PLASTIC*	HNO_3 or HCl (20 Drops/Bottle)*	100	Technicon Auto Analyzer, A.A.S.†
KJELDAHL NITROGEN	- SEE NITROGEN - TOTAL KJELDAHL			
L.A.S.	- SEE ANIONIC DETERGENTS (MBAS)			
LEAD	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.†
LINEAR ALKYL SULFONATES	- SEE ANIONIC DETERGENTS (MBAS)			
LITHIUM	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.†
MAGNESIUM	GLASS OR PLASTIC	NONE*	100	A.A.S. ; calculated
MANGANESE	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.†
MERCURY	GLASS ONLY*	HNO_3-KMnO *	250	Flameless A.A.S. †
METHYLENE BLUE ACTIVE SUBSTANCES	- SEE ANIONIC DETERGENTS (MBAS)			
MOLYBDENUM	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.†
NICKEL	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.†
NITRATE NITROGEN (FILTERED)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE	75	Technicon Auto Analyzer
NITRILOTRIACETIC ACID	GLASS ONLY	Formaldehyde (2 mls/20oz Bottle)	600	Polarography
NITRITE NITROGEN (FILTERED)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE	75	Technicon Auto Analyzer
NITROGEN - AMMONIA	- SEE AMMONIA NITROGEN			
NITROGEN - NITRATE (FILTERED)	- SEE NITRATE NITROGEN (FILTERED)			
NITROGEN - NITRITE (FILTERED)	- SEE NITRITE NITROGEN (FILTERED)			
NITROGEN - TOTAL KJELDAHL	GLASS OR PLASTIC	REFRIGERATE OR FREEZE	75	Technicon Auto Analyzer
N.T.A.	- SEE NITRILOTRIACETIC ACID			
ORTHOPHOSPHATES - FILTERED REACTIVE	GLASS OR PLASTIC	REFRIGERATE OR FREEZE	75	Technicon Auto Analyzer
PESTICIDES	GLASS ONLY	REFRIGERATE	900	Solvent Extraction & Gas Chromatography
PETROLEUM HYDROCARBONS	GLASS ONLY	REFRIGERATE	900	Solvent Extraction & Gas Chromatography
pH	GLASS OR PLASTIC	NONE*	25	Radiometer
PHENOLICS (REACTIVE)	SPECIAL*	PROVIDED*	150	Technicon Auto Analyzer (4AAP); manual GIBBS
PHOSPHORUS - FILTERED REACTIVE	- SEE ORTHOPHOSPHATES - FILTERED REACTIVE			
PHOSPHORUS - TOTAL	GLASS OR PLASTIC	REFRIGERATE OR FREEZE	75	Technicon Auto Analyzer
POTASSIUM	PLASTIC*	NONE	40	A.A.S.†
RESIN AND FATTY ACIDS	GLASS ONLY	REFRIGERATE - NaOH*	900	Solvent Extraction & Gas Chromatography
SELENIUM	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	Fluorometric
SETTLEABILITY	GLASS	NONE	900	Direct Volume measurement
SILICA	- SEE SILICATES - REACTIVE			
SILICATES - REACTIVE	PLASTIC ONLY	NONE	50	Technicon Auto Analyzer
SILVER	PLASTIC & GLASS	HNO_3 (20 Drops/Bottle)	100	A.A.S.†
SLUDGE VOLUME INDEX	NONE*	NONE*	NONE*	Calculated

CHEMICAL PARAMETER	PREFERRED SAMPLING CONTAINER	PRESERVATION TECHNIQUE	MINIMUM VOLUME OF SAMPLE (mls)	ANALYTICAL TECHNIQUE
SODIUM	PLASTIC*	NONE*	40	A.A.S.†
SOLIDS - DISSOLVED	GLASS	REFRIGERATE	75	Gravimetric
SOLIDS - IGNITED	GLASS	REFRIGERATE	200*	Gravimetric
SOLIDS - SUSPENDED	GLASS	REFRIGERATE	200*	Gravimetric
SOLVENT EXTRACTABLES	GLASS	REFRIGERATE	900	Gravimetric with solvent extraction
SPECIFIC CONDUCTANCE	- SEE CONDUCTIVITY			
STRONTIUM	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.
SULFATE	GLASS OR PLASTIC	NONE	50	Technicon Auto Analyzer
SULFIDE	GLASS OR PLASTIC	Na_2CO_3-Zn $(C_2H_3O_2)_2$ Refrigerate*	900	Manual Colorimetry
SUSPENDED SOLIDS	- SEE SOLIDS - SUSPENDED			
TANNINS AND LIGNINS	GLASS	REFRIGERATE ONLY	200	Manual Colorimetry
TITANIUM	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	Manual Colorimetry
TOTAL KJELDAHL NITROGEN	- SEE NITROGEN - TOTAL KJELDAHL			
TOTAL PHOSPHORUS	- SEE PHOSPHORUS TOTAL			
TURBIDITY	GLASS OR PLASTIC	KEEP IN DARKNESS	50	Nephelometric (HACH 1300 or 1300A)
URANIUM	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	Manual Colorimetry
VANADIUM	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.†
VINYL CHLORIDE (MONOMERIC)	SPECIAL*	KEEP IN DARKNESS	10	Gas Chromatography
VOLATILE ACIDS	GLASS	REFRIGERATE	25	Manual NaOH Titration
ZINC	PLASTIC & GLASS*	HNO_3 (20 Drops/Bottle)	100	A.A.S.†

* See Individual Method Outline

† Atomic Absorption Spectrophotometry

TABLE II B

1975 ANALYTICAL SPECIFICATIONS FOR ROUTINE WATER QUALITY PARAMETERS

PARAMETER		RANGE ON UNDILUTED SAMPLE (IN mg/l UNLESS OTHERWISE INDICATED	PRECISION (mg/l)
ACIDITY		4 - 500	±2
ALKALINITY		2 - 800	±1
AMMONIA NITROGEN (FILTERED)	(RANGE I[1])	.01 - 1.0	±.01
	(RANGE II[2])	0.2 - 20	±0.2
ANIONIC DETERGENTS		0.1 - 0.5	±0.1
BIOCHEMICAL OXYGEN DEMAND		0.2 - 10	±0.1
CALCIUM (TITRIMETRIC METHOD)		2 - 200	±1
CARBON		2 - 100*	±1
CARBON DIOXIDE		1 - 88*	±0.5*
CHEMICAL OXYGEN DEMAND		20 - 800	±5
CHLORIDE (TITRIMETRIC METHOD)		4 - 400	±2
(COLORIMETRIC METHOD)	(RANGE I[1])	0.1 - 10	±0.1
(COLORIMETRIC METHOD)	(RANGE II[2])	0.5 - 50*	±0.5*
CHLOROPHYLL (METHOD CHANGED IN 1975)		1 - 8 mg/m^3	±0.5 mg/m^3
COLOR - APPARENT		5 - 250 H.U.	±5 H.U.
CONDUCTIVITY		1 - 1.5×10^7 µmhos/cm	±2 - 5%
FLUORIDE (COLORIMETRIC METHOD)		.04 - 2.0	±.02
(ION SPECIFIC ELECTRODE METHOD)		0.1 - 10	±.05 or ± 5% (whichever is greater)
HARDNESS		4 - 500	±2
IRON - TOTAL (COLORIMETRIC METHOD)		.04 - 2.0	±.02
MAGNESIUM (CALCULATED)		2 - 100	±1
NITRATE NITROGEN (FILTERED)	(RANGE I[1])	.02 - 2.0	±.01
	(RANGE II[2])	0.2 - 20	±0.1
NITRITE NITROGEN (FILTERED)	(RANGE I[1])	.002 - 0.2	±.001
	(RANGE II[2])	.02 - 2.0	±.01
NITROGEN - KJELDAHL	(RANGE I[1])	0.1 - 2.0	±.05
	(RANGE II[2])	0.5 - 10	±.25
ORTHOPHOSPHATE - FILTERED REACTIVE	(RANGE I[1])	.002 - 0.2	±.001
	(RANGE II[2])	0.1 - 10	±.05
pH		Not applicable	±0.1
PHENOLICS - REACTIVE (4AAP METHOD)		2 - 50 µg/l	±0.5 µg/l
PHOSPHORUS - TOTAL	(RANGE I[1])	.004 - 0.2	±.002
	(RANGE II[2])	0.1 - 5.0	±.05
POTASSIUM (A.A.S. METHOD)	(RANGE I[1])	0.4 - 10	±0.2
(A.A.S. METHOD)	(RANGE II[2])	1 - 30	±.05
(FLAME PHOTOMETRIC METHOD)		0.4 - 10	±0.2
SILICATES - REACTIVE		0.1 - 5.0	±.05
SODIUM (A.A.S. METHOD)	(RANGE I[1])	0.4 - 10	±0.2
(A.A.S. METHOD)	(RANGE II[2])	2 - 50	±1
(FLAME PHOTOMETRIC METHOD)		0.4 - 10	±0.2
SOLIDS - DISSOLVED (GRAVIMETRIC METHOD)		50 - Unlimited	±5 or ±5% (whichever is greater)
SOLIDS - IGNITED (GRAVIMETRIC METHOD)		100 - Unlimited	±10%
SOLIDS - SUSPENDED (GRAVIMETRIC METHOD)		4 - 1000	±2 or ±5% (whichever is greater)
SULFATE	(RANGE I[1])	2 - 50*	±1*
	(RANGE II[2])	10 - 250	±5
SULFIDE (METHYLENE BLUE METHOD)		0.2 - 2.0	±0.1
TURBIDITY		.05 - 1000 F.T.U.	±2%
VOLATILE ACIDS		50 - 2500	±25

[1] Routine Range for River and Lake Samples

[2] Routine Range for Domestic Water and Domestic Waste Samples

* See Individual Method Outline

TABLE II C

1975 ANALYTICAL SPECIFICATIONS FOR ROUTINE INORGANIC TRACE CONTAMINANTS

PARAMETER		RANGE ON UNDILUTED SAMPLE (in mg/l unless otherwise indicated)	PRECISION (mg/l)
ALUMINUM		.04 - 2.0	±.02
ARSENIC	(A.A.S. METHOD)	.002 - 0.1	±.001
	(COLORIMETRIC METHOD)	.02 - 1.0	±.01
BARIUM		.02 - 2.0	Not available
BORON		.02 - 1.0	±.01
CADMIUM		.02 - 3.0	±.01
CALCIUM	(A.A.S. METHOD)	.05 - 5.0	±.01
CHROMIUM	(A.A.S. METHOD)	.02 - 2.0	±.01
	(COLORIMETRIC METHOD)	.04 - 20	±.02
COBALT		.07 - 7.0	±.02
COPPER		.05 - 5.0	±.02
CYANIDE	(COLORIMETRIC METHOD)	.02 - 1.0	±.01
	(TITRIMETRIC METHOD)	2 - 50	±1
IRON - TOTAL	(A.A.S. METHOD)	0.1 - 6.0	±.06
LEAD		.04 - 12	±.02
LITHIUM		.02 - 2.0	±.06 (at the 2.0 level)
MAGNESIUM	(A.A.S. METHOD)	.004 - 1.0	±.002
MANGANESE		.04 - 4.0	±.01
MERCURY		.05 - 10μg/l	±.03μg/l* (at the 0.2 level)
MOLYBDENUM		.04 - 10	±.02* (at the 1.0 level)
NICKEL		.0[illegible] - 7.0	±.03
SELENIUM		.002 - 0.2	Not available
SILVER		.04 - 4.0	±.01
STRONTIUM		.01 - 1.0	Not available
SULFIDE	(AMMONIUM MOLYBDATE METHOD)	.02 - 1000	±.02
TITANIUM		.04 - 1.0	±.02 (at the 0.4 level)
URANIUM		.01 - 1.0	Not available
VANADIUM		0.1 - 100	±.05
ZINC		0.5 - 5	±.02 (at the 0.4 level)

TABLE II D

1975 ANALYTICAL SPECIFICATIONS FOR ROUTINE ORGANIC TRACE CONTAMINANTS

PARAMETER	RANGE ON UNDILUTED SAMPLE (in mg/l unless otherwise indicated)	PRECISION (mg/l)
NITRILOTRIACETIC ACID	.05 - 2.5	Not available
PESTICIDES	1.0 - 100 mg/l	±5 - 10%
	(Dependent on compound)	
PETROLEUM HYDROCARBONS	Variable	Not available
PHENOLICS - REACTIVE (GIBBS METHOD)	2 - 120	Not available
RESIN AND FATTY ACIDS	Variable	Not available
SOLVENT EXTRACTABLES	2 - 100	±1
TANNINS AND LIGNINS	1.0 - 10	±1
VINYL CHLORIDE (MONOMERIC)	Not available	±2

* See Individual Method Outline

ACIDITY

The acidity of a water is a measure of its capacity to neutralize base. The major acidic component of natural waters is carbonic acid which is formed by the atmospheric absorption of carbon dioxide or by the release of carbon dioxide as a metabolic by-product. The presence of sulfuric acid, hydrochloric acid, and hydrolyzable metallic salts (primarily those of iron and aluminum) may provide for a "mineral acidity" in water. Drainage from mine tailings, for example, contains large amounts of sulfuric acid and hydrolyzable iron due to the aerobic oxidation of pyrite (iron sulfide) by sulfur bacteria. The presence of a mineral acid is likely the result of industrial activity.

Carbonic acid acidity is present in any water that has a pH between 4.5 and 8.3. Mineral acidity predominates at pH levels below 4.5. Acid waters are objectionable because of their corrosive properties and their ability to inhibit biological activity.

Results for acidity are reported as mg/l of $CaCO_3$. This represents the quantity of base, expressed as calcium carbonate needed to increase the pH of a measured portion of sample to 8.3. Acidity is best interpreted in conjunction with the pH and alkalinity, as well as any other analyses which identify the acidic components of the water.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	None Required (See Below)

Bottles should be filled completely so that no air bubbles remain after the sample is capped. Do not refrigerate as this may cause precipitation of calcium carbonate. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
4 - 500 mg/l	4 mg/l (If pH >8.3 there is no Acidity)	± 2 mg/l

Samples are analyzed titrimetrically with a standard sodium hydroxide solution (carbonate free) to a pH endpoint of 8.3. The acidity is then reported as the amount of calcium carbonate which is neutralized by the alkaline titrant.

Time of Analysis

Approximately 60 acidity determinations may be completed per day.

ALKALINITY

The alkalinity of a water is a measure of its capacity to neutralize acid. In neutral waters the main component of the alkalinity is the bicarbonate ion which may be formed by the action of dissolved carbon dioxide on limestone or other calcium type deposits. When the pH exceeds 8.3, carbonate and hydroxide ions also become components of the alkalinity. Any ion can contribute to the alkalinity provided that its neutralization reaction takes place above the pH of the specified titration endpoint. For example, the hydrolyzable equivalent of silicates, phosphates, arsenates, aluminates and cyanides are all included in the alkalinity measurement.

The alkalinity of a water is generally used to assess the buffering capacity or the water's capability to resist a change in pH. This means that if an acidic waste is discharged to a natural water system, the effect on the water may not result in a pH change, but may be detected as a drop in alkalinity.

Results for alkalinity are reported as mg/l of $CaCO_3$. This does not necessarily imply that there is this much calcium carbonate in the water or that there is any at all. The alkalinity measurement represents the quantity of acid, expressed as calcium carbonate, needed to reduce the pH of a measured portion of sample to 4.5.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	NONE REQUIRED (See Below)

Bottles should be filled completely so that no air bubbles remain after the sample is capped. Do not refrigerate as this may cause precipitation of calcium carbonate. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
2 - 800 mg/l	2 mg/l (if pH <4.5 there is no alkalinity	± 1 mg/l

Samples are titrated automatically on a Titralyzer with a standard sulfuric acid solution to a pH endpoint of 4.5. The alkalinity is then reported as the amount of calcium carbonate which is neutralized by the acid titrant.

Time of Analysis

Approximately 120 alkalinity determinations may be completed per day.

ALUMINUM

Aluminum is one of the most abundant elements in nature and is widely distributed in both soluble and insoluble forms. Its most important sources include bauxite, cryolite, alum, corundum and kaolin minerals. Aluminum compounds occur naturally in water, but may also be derived from industrial wastes or effluents from water treatment plants where alum is commonly used as a precipitating or flocculating agent. The presence of small amounts of aluminum in water may interfere with certain industrial processes.

At present, there is no evidence that aluminum is physiologically harmful and no drinking water objective has been specified. Toxic effects on plants have been reported for extreme conditions at both ends of the pH scale, but at a neutral pH, toxicity effects are negligible.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* Acid Washed PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass bottles are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
A.A.S. .04 - 2.0 mg/l	.04 mg/l	.02 mg/l (at the Detection Limit) .06 mg/l (at the 1.0 mg/l level)

Analysis is accomplished by atomic absorption spectrophotometry using a nitrous oxide-acetylene flame.

Time of Analysis

Time of analysis depends on the amount of preparation work required. Approximately 32 analyses may be performed per day on undigested samples whereas 16 analyses may be performed per day on digested samples.

AMMONIA NITROGEN-FILTERED

(FREE AMMONIA)

Ammonia nitrogen is commonly encountered in domestic wastewater and industrial effluents. It is also found as a biochemical reduction product in ground water.

Ammonia nitrogen is undesirable because it is toxic to fish, exerts a high oxygen demand when converted to nitrite and nitrate, and interferes with water treatment procedures by reacting with chlorine to form chloramines. The latter reaction greatly reduces the effectiveness of the chlorination process. It is also objectionable because its nutritive properties promote the excessive growth of algae and other aquatic plants. Ammonia is rarely found in concentrations high enough to be harmful to humans.

Ammonia results are of great value in interpreting the effectiveness of the waste stabilization process at sewage treatment plants. The relative abundance of ammonia in the treated water is an indication of how far treatment has progressed.

Ammonia is rather short lived in surface waters; therefore, it may not reveal the complete extent of pollution. Results must be interpreted with full allowance for its perishability, both in situ and in the sample following collection.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Ammonia is unstable and rapidly converted to other nitrogen compounds by bacterial activity. Samples must be refrigerated or frozen immediately after collection and delivered to the laboratory as soon as possible.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.01 - 1.0 mg/l	.01 mg/l	± .01 mg/l

Samples are pretreated by filtration and analysis is accomplished colorimetrically by the alkaline phenol hypochlorite method using an Auto Analyzer system. High levels of manganese, cobalt, iron, trivalent chrome, and calcium are known to produce interferences. Ammonia results are reported in mg/l of nitrogen.

Time of Analysis

Approximately 200 ammonia analyses may be performed during an 18 hour Auto-Analyzer working period.

25/2/75

ANIONIC DETERGENTS
(Methylene Blue Active Substances)

Anionic detergents are generally sodium salts of complex organic compounds of the sulfate and sulphonate variety. All are readily soluble in water and ionize to produce the sodium cation and a negatively charged surface active organic ion. They are commonly referred to as "surfactants" because of their ability to reduce the surface tension of water.

Anionic detergents are not found in nature; therefore the presence of these substances in natural waters indicates contamination by domestic or industrial wastes. While generally considered non-toxic to most life forms at low levels, they are objectionable because they cause excessive foaming and inhibit the normal exchange of atmospheric oxygen with water.

The test for anionic detergents is more accurately referred to as "methylene blue active substances" (MBAS) since any material which forms a colored complex with methylene blue will be detected. As the reported result probably represents an overestimate of the anionic detergent concentration, caution should be exercised in interpreting the data. Samples which do not produce any foam when shaken contain less than 0.5 mg/l of MBAS as LAS (Linear alkyl sulfonates). Since this is the objective for natural waters, it is not necessary to request a MBAS analysis on samples when a perceptible foam does not appear.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation [illegible]
100 mls (4 ounces)	GLASS	REFRIGERATE

MBAS are unstable and will be degraded rapidly by bacterial activity. Refrigeration is helpful and immediate delivery to the laboratory is essential. Care must be taken to avoid contamination of the sampling containers by any detergent product used for cleaning.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 0.5 mg/l	0.1 mg/l	± 0.1 mg/l

Samples are mixed with a methylene blue reagent and any substances in the sample which are methylene blue active will be extracted as blue colored salts in chloroform (they are more soluble in chloroform than in water). The chloroform layer is then analyzed colorimetrically using LAS* as the calibration standard. Results are reported in mg/l of MBAS as LAS.

Time of Analysis

Approximately 36 MBAS analyses may be completed per day.

*Reference LAS solutions with a mean molecular weight of 318 and an activity of 5.55% are prepared by the U.S. Environmental Protection Agency in co-operation with the Soap and Detergent Association.

ARSENIC

Arsenic is commonly found in nature as the minerals realgar, orpiment, arsenolite, mispickel and arsenopyite. Arsenic may be present in natural waters by dissolution of these minerals, industrial discharges, and pesticide application. Common industrial applications include the processing of metal ores, glassware, ceramics and tannery products. Manufactured products containing arsenic include wood preservatives, herbicides and insecticides.

As a pollutant in water, arsenic is commonly found as the inorganic oxyanious arsenite and aresenate, as the gas arsine, and as organic arsenicals such as methyl arsenate, phenyl arsenate and trimethylarsine.

The element and its inorganic salts are highly toxic to humans and are known to exhibit carcinogenic properties especially in the arsenate form. Since arsenic is eliminated from the body very slowly, it tends to accumulate, becoming concentrated in the nails, hair, and skin. Hence the prolonged intake of water containing only minute quantities of arsenic may be a health hazard. For this reason, the maximum permissible concentration in domestic water supplies has been established as 0.05 mg/l, with an objective of less than 0.01 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	PLASTIC OR GLASS	NONE REQUIRED (Acid Preserved Samples Acceptable)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard deviation)
A.A.S. .002 - 0.1 mg/l	.002 mg/l	± .001 mg/l
Colorimetric .02 - 1.0 mg/l	.02 mg/l	± .01 mg/l

1) Arsenic is converted to a suitable oxidation state by digestion with a nitric-sulfuric acid mixture, converted to arsine by reduction with sodium borohydride, and analyzed spectrophotometrically by a flameless atomic absorption technique (Toronto laboratory).

2) Arsenic is converted to a suitable oxidation state by digestion with a nitric-sulfuric acid mixture converted to arsine by reduction in a modified Gutzeit generator and analyzed colorimetrically using silver diethyldithiocarbamate (Thunder Bay laboratory).

Several metals may interfere but the principal interference for both techniques is antimony.

Time of Analysis

Approximately 50 arsenic analyses can be completed per day by atomic absorption and 15 per day by colorimetry.

25/2/75

BARIUM

Barium is commonly found in nature as the minerals barite (barium sulfate) and witherite (barium carbonate). It is also found in igneous rock, primarily feldspar, where it is known to replace potassium. The presence of barium in water is very rare unless originating in an industrial discharge. Industrial application of barium includes the manufacture of metal alloys, paints, pigments, paper, soap, rubber, linoleum, flares, cement and various other products.

Insoluble barium salts are relatively non-toxic. Barium sulfate, for example, is used as a contrast material in the radiological diagnosis of ulcers. Soluble salts of barium, however, are readily absorbed through the skin or gastro-intestinal tract and exhibit highly toxic effects on the nervous system if present in sufficient quantity. Symptoms include violent muscular spasms, paralysis and cardiac arrest. Trace quantities of soluble barium are known to accumulate in bones, but are not believed to exhibit a cumulative toxic effect like lead or cadmium. The maximum acceptable concentration of barium in a domestic water supply is 1.0 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* Acid Washed PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass bottles are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 2.0 mg/l	0.2 mg/l	Presently Not Available

Samples are digested with a nitric-hydrochloric acid mixture and analysis is accomplished by atomic absorption spectrophotometry using a nitrous oxide-acetylene flame. The analysis is subject to several positive interferences which reduce the experimental precision.

Time of Analysis

Approximately 50 barium analyses may be completed per day.

BIOCHEMICAL OXYGEN DEMAND (BOD_5)

The BOD_5 test is defined as the measure of dissolved oxygen required for the aerobic bacterial stabilization of decomposable organic matter in a five day period at 20°C in the absence of light.

The most frequent damage caused by the discharge of wastes to natural waters, is the reduction of dissolved oxygen concentrations to levels which cannot support normal aquatic life. This oxygen depletion arises via the bacterial oxidation of organic material and eventually leads to a general deterioration of water quality for all uses. Ideally the BOD_5 should be supplemented by on-site dissolved oxygen measurements in order to assess the effects of stream conditions which offset or accentuate the utilization of dissolved oxygen.

The precision of the method is seriously reduced if the sample contains large fragments of suspended solids or an immiscible layer of oil. Representative portions of such samples cannot be properly aliquoted and the results are not generally reproducible within acceptable limits.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
500 mls (18 ounces)	GLASS	REFRIGERATE

The BOD_5 is a perishable quantity since it is readily influenced by bacterial activity. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.2 - 10 mg/l of Oxygen	0.2 mg/l of Oxygen	± 0.1 mg/l of Oxygen

Dilutions are prepared on the original sample as necessary, and the dissolved oxygen depletion measured after a five day incubation period in a sealed bottle at 20°C. Only those dilutions which give a dissolved oxygen depletion between 25 and 75% are accepted for calculating the BOD_5. Dissolved oxygen levels are measured using a membrane electrode polarograph which is calibrated via the Winkler Method (1). Samples with high chlorine residuals and adverse pH levels are chemically adjusted to remove these toxic influences and are then seeded with sewage.

Time of Analysis

By definition, the BOD_5 test will take five days to complete. However, approximately 250 BOD_5 analyses may be set up per day.

BORON

Boron occurs in nature as the minerals borax, colemanite, boronatrocalcite, and boracite. These mineral deposits may significantly increase the boron concentration in natural waters, but the presence of boron is most likely due to the disposal of cleaning agents in urban sanitation systems or the discharge of industrial effluents. In both natural and industrial cases boron will likely be found as the borate anion. Boron is used in industry as a neutron absorber and shielding material in nuclear power plants, as a hardening constituent in steel alloys, as a fire proofing agent, and in the manufacture of glass, porcelain enamels, detergents, pharmaceuticals, abrasives, dyes and high energy fuels.

Boron is an essential trace element for plant growth, playing a significant role in respiratory processes and the breakdown of carbohydrates. No similar function has been discovered in animals.

Boron is toxic to both animals and plants at high concentrations. Symptoms of boron poisoning in humans include abdominal pain, nausea, and diarrhea. Death occurs as a result of central nervous system paralysis. The maximum permissible concentration of boron in a domestic water supply is 1.0 mg/l. However, boron very seldom exceeds a concentration of 0.1 mg/l

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC ONLY	NONE REQUIRED

Glass containers should not be used since boron is a major component of glass.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 1.0 mg/l	.02 mg/l	± .01 mg/l

Samples are acidified and evaporated to dryness in the presence of curcumin to produce a red colored derivative known as rosocyanine which is then analyzed colorimetrically. A Nitrate concentration in excess of 20 mg/l as N. causes an interference.

Time of Analysis

Approximately 15 boron analyses may be completed per day.

CALCIUM

Calcium ranks fifth in the order of natural elemental abundance and is commonly found in deposits of limestone, dolomite, gypsum, and gypsiferous shale. It is generally present in all natural waters at levels which depend on the amount of contact with specific geological formations. For this reason, surface water tends to be lower in calcium than ground water.

Calcium is an essential element for all life forms. In plants, it is known to enhance biological productivity; in animals, it is necessary for proper bone and teeth formation. Aqueous calcium compounds are generally non-toxic and represent no known health hazard.

Small concentrations of calcium assist in preventing the corrosion of metal pipes by forming a protective layer of calcium carbonate; however, large concentrations cause excessive scale which leads to restricted flow and pressure build-ups. Calcium is the major contributor to water "hardness". (See Hardness).

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	GLASS OR PLASTIC	None * Required

*Non-routine industrial waste samples, or any other samples where high levels of heavy metals are suspected, should be sampled in plastic containers and preserved with 20 drops of nitric acid per bottle.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Titrimetric 2 - 200 mg/l	2 mg/l	± 1 mg/l
A.A.S. .05 - 5.0 mg/l	.05 mg/l	± .01 mg/l

Samples are either buffered to a pH of 12-13 and titrated with ethylenediaminetetraacetic acid (EDTA) to the Murexide endpoint or analyzed for calcium using atomic absorption spectrophotometry.

Time of Analysis

Approximately 70 calcium analyses may be completed per day using the titrimetric method and 50 per day using the atomic absorption method.

CADMIUM

The principal source of cadmium is the mineral greenockite which may contain up to 77% of the element. Industrial applications of cadmium and its salts include metallurgy, electroplating and the manufacture of pigments and insecticides. Cadmium is rarely found in natural waters, hence its presence is usually due to an industrial discharge or the deterioration of galvanized pipe.

All forms of cadmium are highly toxic, and once ingested are likely to remain in the body for a long time, becoming concentrated in the liver, kidneys and other organs. Cases have been reported where toxic effects did not become apparent until many years after the last exposure. The water quality criteria for cadmium in domestic water supplies is .01 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	Acid Washed PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

When levels below the normal range of application are required, a notation must be included on the sample submission form so that the sample will be preconcentrated prior to analysis. One full 32oz. bottle is required exclusively for the preconcentration process.

Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 3.0 mg/l	.02 mg/l	±.01 mg/l

Samples are digested using a mixture of nitric-sulfuric acid and then analyzed by atomic absorption spectrophotometry. Cadmium is one of the elements most suited to atomic absorption analysis as there are no known chemical or spectral interferences.

Time of Analysis

Approximately 50 cadmium analyses may be completed per day.

25/2/75

CARBON

(Total, Organic and Inorganic)

Both total carbon and inorganic carbon are determined by direct analysis on a liquid sample. The organic carbon component is obtained by taking the difference between the total carbon and the inorganic carbon. The total organic carbon generally relates directly to the BOD and COD, but this relationship depends upon the nature of the organic material in the sample.

Carbon analyses are rapid and relatively simple to perform. The TOC is often preferred to the BOD and COD because it relates more directly to the organic content of a water. It is commonly used to assess the efficiency of waste stabilization processes and the degree of organic pollution in receiving waters. Inorganic carbon results are essential in calculating the biological productivity of a water.

The presence of suspended solids in a water sample decreases the precision of the analysis. Only a supernatant analysis is performed unless otherwise requested.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls	GLASS OR PLASTIC	REFRIGERATE

Containers should be filled completely so that no air bubbles remain once the sample is capped. Since production of CO_2 and the interconversion of carbonaceous substances via bacterial activity is likely, immediate delivery to the laboratory is essential.

A non-routine modification has been developed to extend the detection limit down to 0.1 mg/l. Applications include rainwater analysis and special studies. Laboratory staff should be consulted if low level measurements are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
2 - 100 mg/l	2 mg/l	± 1 mg/l

Total carbon is determined by injecting a known volume of sample onto a hot catalyst using a hypodermic syringe. The CO_2 gas produced on combustion is measured by infra-red spectrophotometry. Inorganic carbon is determined by acidifying a known volume of sample in a closed chamber and the released CO_2 gas measured by infra-red spectrophotometry. Results are reported in mg/l of carbon.

Time of Analysis

Approximately 60 carbon analyses may be completed per day.

25/2/75

CARBON DIOXIDE

Dissolved carbon dioxide (carbonic acid) is generally found in all water samples with a pH between 4.5 and 8.3. Surface water contains dissolved CO_2 as a result of atmospheric absorption. Ground waters and waters from the hypolimnion of stratified lakes and reservoirs contain dissolved CO_2 as a result of bacterial activity.

Since the dissolved carbon dioxide determination has many sources of error, caution must be exercised in its interpretation. It is an acidity measurement and will include all forms of acidity, not only CO_2. Samples with a pH close to 4.5 may produce CO_2 results which are really the sum of the carbonic acid acidity and a portion of the mineral acidity. Any changes in temperature or barometric pressure are likely to change the CO_2 content of the sample.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
Full Special Container	Special Glass Bottle (See Below)	(See Below)

Special precautions are required to minimize agitation of the sample otherwise CO_2 will be lost. Samples are to be carefully transferred from the sampling device into the bottom of a special leak proof glass stoppered container via a syphon. Allow plenty of sample to overflow before the container is finally capped. If any air bubbles remain in the container, analysis cannot be performed. Samples should then be refrigerated and brought to the laboratory within 24 hours. Samplers generally deliver CO_2 samples personally as they are unsafe to ship commercially.

Consultation with laboratory staff is required prior to sampling as special preparations are necessary before the samples arrive. Field determinations are recommended when possible.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1.0 - 88 mg/l	1.0 mg/l	± 0.5 mg/l

Samples are transferred by syphon to Nessler tubes where they are titrated potentiometrically with carbonate free sodium hydroxide to a pH endpoint of 8.3. Special precautions are practised to limit any errors due to atmospheric exchange of CO_2. Results are reported in mg/l of CO_2.

Time of Analysis

Approximately 40 CO_2 analyses may be completed per day.

CHEMICAL OXYGEN DEMAND (COD)

The chemical oxygen demand is a measure of the oxygen required to oxidize susceptible organic and inorganic compounds under vigorous chemical oxidizing conditions. This test is especially useful on industrial wastes where the BOD_5 test is not applicable. Toxic materials in industrial wastes tend to inhibit bacterial activity producing a BOD_5 which generally underestimates the true organic composition of the sample. Most organic compounds are oxidized by the COD method; the most common exceptions are benzene, toluene, pyridine, and similar aromatic ring compounds. Ammonia and organic nitrogen do not react in this test.

COD results do not necessarily relate directly to the BOD_5 value or to the oxygen consumption in the receiving water, but they do represent the ultimate carbonaceous oxygen demand that may eventually be exerted. If a number of comparative analyses show that a stable ratio exists between the COD and BOD for a particular waste, then the COD results may be used to predict the approximate BOD values.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
25 mls (1 ounce)	GLASS	REFRIGERATE

The COD is a perishable quantity since it may be influenced by bacterial activity. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
20 - 800 mg/l of Oxygen	20 mg/l of Oxygen	± 5 mg/l of Oxygen

A water sample is refluxed with a known amount of potassium dichromate and sulfuric acid for two hours. Mercuric sulfate is added to prevent chloride interference, and silver sulfate is added to catalyze the oxidation of straight chain hydrocarbons. The oxygen utilized by the sample is determined by titration with ferrous ammonium sulfate and results are reported in mg/l of oxygen.

Time of Analysis

Approximately 65 COD analyses may be completed per day.

25/2/75

CHLORIDE

Chloride is a major anion in domestic wastes and in many natural water supplies. Urban runoff often contains high concentrations of chloride in the winter time due to road application of salt.

Chloride poses no direct health hazard, but the water quality objective for domestic water supplies has been specified at 250 mg/l to prevent a salty taste. This salty taste is variable and dependent on the composition of the water. If chloride is present as sodium chloride, a detectable taste will be present at 250 mg/l. If chloride is present as calcium or magnesium chlorides, waters containing as much as 1000 mg/l may not have a noticeable taste.

The chloride method actually measures the total chloride, bromide, iodide, and cyanide concentration. Therefore, caution must be exercised in interpreting the chloride results. In the case of natural fresh waters, the concentrations of bromide, iodide, and cyanide are negligible and the result will closely represent the chloride content of the sample. In regions of Northern Ontario where watercourses are influenced by Arctic tidewater, this is not the case.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS	None Required

A non-routine modification has been developed to extend the detection limit down to .02 mg/l. Applications include rainwater analysis and special studies. Laboratory staff should be consulted if low level measurements are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Titrimetric 4 - 400 mg/l	4 mg/l	± 2 mg/l
Colorimetric 0.1 - 10 mg/l	0.1 mg/l	± 0.1 mg/l

1) Samples are titrated automatically on a Titralyzer instrument using a standardized silver nitrate solution.

2) **Samples** are analyzed colorimetrically by reacting chloride with mercuric thiocyanate in the presence of excess ferric iron to produce the colored ferric thiocyanate complex which is proportional to the original chloride concentration.

Sulfide, thiosulfate, sulfite, orthophosphate, bromide, iodide and cyanide are known interferences.

Time of Analysis

Approximately 120 chloride analyses may be completed per day titrimetrically and 200 per day colorimetrically.

25/2/75

CHLOROPHYLL

Chlorophyll is the natural pigment component of all green plants. The quantity of chlorophyll in a water sample is therefore a good indication of how much plant material is present. More specifically, chlorophyll data provides a way to estimate the biomass of standing algae crops which can then be used to assess the effectiveness of nutrient removal programs as well as the general trophic status of lakes and rivers.

Chlorophyll results are normally reported as "chlorophyll a", "chlorophyll b" and "acidified chlorophyll a". Generally the "acidified chlorophyll a" result is considered most useful because it represents the pigment contribution of living cells. "Chlorophyll a" represents the total pigment contribution of both living and dead cells (degraded chlorophyll pigments in dead cells are called pheophytins). "Chlorophyll b" is often very small relative to "chlorophyll a", therefore its interpretive value is limited. As the anlytical variability becomes very large for high concentrations of chlorophyll, caution should be exercised in interpreting results where the "chlorophyll a" exceeds 20 µg/l

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (32 ounces)	NONE - Field Filtration is Recommended (See Below)	10% $MgCO_3$ at 1 ml Per Litre of Sample

Add one ml of a 10% $MgCO_3$ suspension to about one litre of sample. This prevents the conversion of chlorophyll to pheopigments at low pH levels. Filter a measured aliquot (approximately one litre) through a 1.2 micron cellulose nitrate membrane filter. Place the filter in a labelled petrie dish being sure to include the exact volume of the filtered aliquot on the label. Wrap the petrie dishes in aluminum foil and ship to the Laboratory for analyses.

If filtration in the field is not possible, efforts must be made to retard photosynthetic activity. Samples should be taken in glass bottles, refrigerated and kept in the dark. Immediate delivery to the Laboratory is essential.

Method

Range of Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1 - 8 mg/m^3 –same as µg/l	1 mg/m^3	± 0.5 mg/m^3

Chlorophyll is extracted with 90% acetone and analysis accomplished spectrophotometrically. The final result is mathematically determined by considering absorbance readings at four different wavelengths. Any substance which absorbs light at the analysis wavelengths will be detected as an interference.

Time of Analysis

Approximately 100 chlorophyll analyses may be completed per day.

CHROMIUM

Chromium occurs in nature primarily as chromite or chrome iron ore. Hexavalent chromium compounds have extensive industrial applications especially in the plating and tanning industries. They are also used in the manufacture of paints and dyes. The trivalent form of chromium is used to a much lesser extent. The presence of chromium in water is usually the result of an industrial discharge or the discharge of cooling waters in which chromium has been utilized as a corrosion inhibitor.

Chromium is present in small quantities in all soils and plants, but there is no evidence to indicate that it is required by plants for growth. Soils with a high chromium content are generally infertile. Hexavalent chromium is the most toxic inorganic form of the element and has been demonstrated to exhibit carcinogenic properties. The maximum permissible concentration in domestic water supplies has been established at 0.05 mg/l of hexavalent chromium.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	*ACID-WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle) No Preservative for Hexavalent Chrome

Fill bottle completely to the top and deliver to the laboratory as quickly as possible. Chromate ion is readily adsorbed on container surfaces and delays in shipment longer than 2 to 3 days may cause erroneous results.

* Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
A.A.S. .02 - 2.0 mg/l	.02 mg/l	± .01 mg/l
Colorimetric .04 - 20 mg/l	.04 mg/l	± .02 mg/l

For a total chromium analysis, the sample must first be digested with sulphuric and nitric acids and hydrogen peroxide; then the chromium is oxidized with permanganate to the hexavalent form. Once in this form, the chromium concentration can be determined by the colorimetric diphenylcarbazide method or by atomic absorption spectrophotometry. Hexavalent chromium is determined directly by the diphenylcarbazide method with no sample pre-treatment other than filtration. High levels of chloride, vanadium, iron, and mercury are known to interfere with the colorimetric method.

Time of Analysis

Approximately 18 chromium analyses may be completed per day by either the colorimetric or atomic absorption methods when analyzed in batches. More hexavalent chrome determinations may be performed per day because of the minimum amount of preparation required.

COBALT

Cobalt is found in nature in the minerals cobalite, smaltite, and erythrite. It is widely used in the manufacture of alloys and pigments used in glass staining. Recently it has found use as a binder in the tungsten carbide tool industry where it is commonly added to steel as a means of improving the cutting quality of certain tools.

Cobalt is an essential element at trace levels for both animal and plant nutrition. It is known to be one of the main constituents of Vitamin B_{12} and its presence is believed to be instrumental in the natural synthesis of this vitamin. Cobalt deficiency in man and animals results in a type of anaemia which may be corrected by administering small dosages of cobalt chloride orally. Adverse effects due to cobalt are very slight even at high concentrations. Nausea and diarrhea are the common symptoms. No limits have been set on the maximum acceptable concentration for cobalt in domestic water supplies. Tentative limits suggested by the Water Quality Criteria are 0.2 mg/l for continuous irrigation of all soils and 10 mg/l for short term use on fine textured soils.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	*ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass bottles are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.07 - 7 mg/l	.07 mg/l	± .02 mg/l

Samples are digested with a nitric-sulfuric acid mixture and analysis is accomplished using atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 cobalt analyses may be completed per day.

COLOR - APPARENT

Color in natural surface waters is primarily associated with the presence of humic acids derived from the decomposition of plant material such as plankton, aquatic macrophytes, terrestrial leaves, and logs. Lakes containing these colored substances are commonly referred to as "acid-bog" or "brown-water" lakes. In ground waters, the color is more likely due to the presence of iron and manganese. In either case, the color is characteristically manifested as varying hues of yellowish-brown.

Waters with colors of unusual hues, such as those of industrial origin, may differ greatly from the typical yellowish-brown color of natural water. Special samples known to contain organic dyes, colored metallic compounds and other types of industrial effluents cannot be adequately assessed using this particular analytical technique.

Only the "apparent color" is reported since it is considered most representative of field conditions. "Apparent color" includes the color due to dissolved substances as well as the additional color contributed by suspended matter. "True color" only considers dissolved colored substances.

Waters colored naturally by humic substances are considered unacceptable for drinking purposes because of their appearance. If the color is due to the presence of iron and manganese, it can also be associated with taste and staining problems. Most naturally colored waters are harmless; hence the specified objective of 5 Hazen Units for domestic supplies is based on aesthetic considerations rather than on known health standards.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS	REFRIGERATE

The color of a water is greatly dependent on changes in pH, the extent of biological activity, and the precipitation of iron and manganese. To minimize changes during transit, sample containers should be filled to the neck, sealed tightly and refrigerated. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
5 - 250 H.U.	5 H.U.	± 5 H.U. (in the 5-20 range)

A sample is visually compared with the color of standardized glass color disks calibrated in Hazen Units (H.U.) using a Lovibond Nesslerizer. The reported result is the Hazen value assigned to the disk which best matches the color of the sample.

Time of Analysis

Approximately 100 color analyses may be completed per day.

CONDUCTIVITY

Conductivity* is defined as the reciprocal of a water's electrical resistance measured between two electrodes one square centimeter in area and one centimeter apart. As a temperature change of $1^{o}C$ will affect the conductivity by approximately 2%, all results are reported relative to a standard temperature of $25^{o}C$.

Any water containing ionized substances will conduct an electric current. Most inorganic acids, bases and salts are good conductors while many organic compounds undergo minimal ionization in aqueous solution. In natural waters the conductivity is mainly due to calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate and nitrate ions. The conductivity contribution of the hydrogen ion is negligible for neutral waters but becomes increasingly significant as the pH decreases below 5.

Conductivity can be correlated with the dissolved solids content. Ontario rivers and lakes, free of industrial wastes, have a dissolved solids concentration equal to 0.65 ± 0.10 times the conductivity. The conductivity method for determining dissolved solids is presently used on a large number of natural water samples (see dissolved solids).

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS	NONE REQUIRED

Care must be taken to avoid contact with any material which can release or absorb ions. Samples should not be frozen as some carbonates are precipitated and not easily redissolved.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
$1 - 1.5 \times 10^{7}$ Micromhos/cm	1 micromhos/cm	± 2 - 5%

The electrical resistance of the sample is measured by an instrument which takes the reciprocal automatically. A water bath is used to adjust the sample's temperature to $25^{o}C$ before a measurement is taken.

Time of Analysis

Approximately 250 analyses may be completed per day.

* NOTE: "Conductivity" and "specific conductance" are often used synonymously.

25/2/75

COPPER

Copper occurs naturally as the free native metal as well as in malachite, cuprite, chalcopyrite and various mixtures of sulfide ores. The presence of copper in natural waters is generally due to industrial activity, but in certain circumstances, copper salts may be introduced to a water distribution system or reservoir as a means of controlling objectionable algae slimes.

Copper is an essential element to the human body, acting as a catalyst in many biochemical reactions. It is generally agreed that copper is an active agent in the synthesis of hemoglobin and that a copper deficiency in animals causes a severe anaemia similar to iron deficiency anaemia. A daily intake of about 2 mg is required for normal body functions. Excessive amounts of copper are toxic, and cause abdominal pain, vomiting and convulsions. Prolonged exposure results in liver and kidney damage. Copper imparts a disagreeable taste to water at concentrations well below those which would be hazardous to health; hence the drinking water standard of 1.0 mg/l is based on taste rather than on toxicity.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

*NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 5 mg/l	.05 mg/l	± .02 mg/l

Samples are first digested with nitric and sulfuric acid and then analyzed using atomic absorption spectrophotometry. High concentrations of sodium and/or potassium (0.5%) interfere with the copper analysis. Laboratory staff should be warned if such concentrations are suspected.

Time of Analysis

Approximately 50 copper analyses can be completed per day.

CYANIDE

Cyanides are a class of chemical compounds which contain a carbon-nitrogen constituent commonly referred to as the cyanide group. Cyanides vary in their degree of chemical activity depending on how readily they dissociate in water to form the cyanide ion. Simple cyanides of the alkali metals readily form this ion while many metal cyanides do so at a much slower rate or not at all.

The presence of cyanide in natural waters is the result of an industrial discharge. Waters containing this substance are extremely toxic to virtually all aquatic life forms and are unsafe for human consumption. Cyanide exerts its toxic effects by inhibiting the normal oxidation processes in body tissue thus causing asphyxiation and death. The maximum acceptable cyanide concentration for domestic water supplies in Ontario has been set at 0.01 mg/l of cyanide as HCN.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
500 mls (18 ounces)	GLASS OR PLASTIC	1 ml of 50% NaOH Per Bottle REFRIGERATE

A sample suspected of containing cyanide should never be acidified, as this will release highly toxic cyanogen gas.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Colorimetric .02 - 1.0 mg/l	.02 mg/l	± .01 mg/l
Titrimetric 2 - 50 mg/l	2 mg/l	± 1 mg/l

All samples are distilled prior to analysis to remove interferences. If an analysis for the ionic or "free cyanide" is required, the sample is distilled from a weakly acidic tartaric acid solution. If a "total cyanide" analysis is required, the sample is distilled under reflux from a solution containing strong acid and metal salts (Serfass Distillation). Samples with more than 1 mg/l of HCN are determined titrametrically using silver nitrate, while samples with less than 1 mg/l of HCN are determined colorimetrically using chloramine-T and barbituric acid reagent. Results are reported in mg/l of HCN.

Time of Analysis

Approximately 16 "free cyanide" analyses may be completed per day, while only 2 "total cyanide" analyses may be completed per day.

FLUORIDE

Fluoride occurs naturally in the minerals fluorspar, fluoroapatite and cryolite, but its presence in natural water is generally due to the fluoridation of domestic water supplies. Fluoride is used in industry for a variety of manufacturing processes such as adhesives and metallurgical fluxes; thus in some instances, its presence may also be due to an industrial discharge.

The Water Quality Criteria for fluoride in domestic water supplies has been set at 1.0 ± 0.2 mg/l for artifically fluoridated water and less than 2.4 mg/l for natural fluoride. Fluoride concentrations near 1.0 mg/l are beneficial in preventing tooth decay. Concentrations slightly in excess of 2.4 mg/l may cause tooth mottling. Excessively high concentrations near 50 mg/l are toxic.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	NONE REQUIRED

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Colorimetric 0.4 - 2.0 mg/l	0.4 mg/l	± 0.02 mg/l
Electrode 0.1 - 10 mg/l	0.1 mg/l	± .05 mg/l or ± 5% (whichever is greater)

Samples are distilled and colorimetrically analyzed on an Auto Analyzer system via the formation of a ternary alizarin blue-lanthanide-fluoride complex or by an ion specific electrode technique using CDTA as an interference suppressant (London laboratory).

Colorimetric kits employed in water works laboratories can give slightly biased results especially if alum treatment is employed. Aluminum is a major interference which tends to depress the detected fluoride concentration. If the presence of aluminum is ignored, there may be a tendency to overfluoridate a water supply. In the case of the alizarin blue method, a 20% depression in the colorimetric response was observed for an undistilled 1.0 mg/l fluoride standard if 0.6 mg/l of aluminum was present. In the case of the ion specific electrode - CDTA method, a 5% depression in the electrode response was observed for an undistilled 1.0 mg/l fluoride standard if 1.0 mg/l of aluminum was present. Distillation is the most effective way of removing the aluminum interference, but this is impractical in most water works laboratories. Generally, corrections may be applied by relating the test kit result to the known fluoride dosage providing the aluminum concentration remains constant.

Time of Analysis

Approximately 100 samples may be analyzed per day.

HARDNESS

The total hardness measures the "soap consuming power" of a water due to the presence of metallic cations. The principal components of the hardness are calcium and magnesium although a number of heavy metals may contribute to a small extent. The hardest waters are usually encountered in regions with thick topsoil layers and extensive limestone deposits.

Hard waters are objectionable because they form insoluble compounds or "curds" with soap. This substantially reduces the efficiency of washing procedures even when detergents are used. Larger quantities of soap are generally required for optimum cleansing in hard water, thus making the washing process considerably more expensive. Hardness in drinking water is limited indirectly by the criteria for dissolved solids (maximum of 500 mg/l).

Hardness has often been measured as a general indication of a water's mineral content. Waters with a high hardness are known to cause the formation of a lime scale in plumbing fixtures. It is therefore especially important to monitor the hardness of industrial water sources where high temperature equipment such as heat exchangers, boilers, steam turbines, hot water pipes, etc., are commonly employed.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	None Required

Sample containers must be filled completely such that no air bubbles remain once they are capped. This precaution will prevent the loss of dissolved carbon dioxide which is essential for keeping calcium carbonate in solution. Samples should not be refrigerated as this will cause the precipitation of calcium carbonate.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
4 - 500 mg/l	4 mg/l	± 2 mg/l

Samples are buffered to a pH of 10 and titrated with ethylenediaminetetraacetic acid (EDTA) to the Eriochrome Black T endpoint. Heavy metals interfere by masking this endpoint; however, suppression techniques are available. Results are reported in mg/l of calcium carbonate.

Time of Analysis

Approximately 70 hardness determinations may be completed per day.

IRON (TOTAL)

Iron is the most abundant of the heavy metals in nature, but is generally found at low levels in most surface waters because of the relatively low solubility of ferric iron when the pH exceeds 7. Compounds of iron in water are in a state of dynamic chemical equilibrium caused by bacterial activity and chemical oxidation. Because the relative concentrations of these compounds are constantly changing, only a total iron determination provides relevant data. The most common forms of iron in water include ferrous ions, ferric ions, inorganic and organic chelates, complex colloidal organics, suspended oxides and hydroxides.

The role of iron is important in eutrophication studies as it affects retention and release mechanisms of phosphorus components in lake and river sediments. This ability of iron to bind up phosphorus is also important in nutrient removal programs at Water Pollution Control Plants where ferric chloride is sometimes used as a phosphate precipitant.

Iron is an important component of hemoglobin and an essential element for all life forms. It is non-toxic at high levels but objectionable in domestic supplies because of the color and bitter taste it imparts. It is also known to cause reddish-brown stains on plumbing fixtures and laundry. The water quality objective for iron in domestic water supplies is 0.3 mg/l (filterable). *

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	GLASS OR PLASTIC	A.A.S. - HNO_3 (20 Drops/Bottle) Colorimetric - HCl (20 Drops/Bottle)

* NOTE: Only a total iron analysis can be determined routinely. If filterable iron is required, samplers must request a total iron analysis on a field filtered sample.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
A.A.S. 0.1- 6.0 mg/l	0.1 mg/l	± .06 mg/l
Colorimetric .04 - 2.0 mg/l	.04 mg/l	± .02 mg/l

Samples are digested with a hydrochloric acid-hydroxylamine mixture and colorimetrically analyzed via an automated orthophenanthroline method. Interferences include strong oxidizing agents, cyanides, nitrites, polyphosphates, chromium, zinc, cobalt, copper and nickel. Fortunately these substances are not common in natural waters, but may be abundant in industrial effluents. In order to minimize this interference problem, industrial waste samples are analyzed for iron using atomic absorption spectrophotometry.

Time of Analysis

Approximately 175 analyses can be performed per day using the colorimetric method and 50 analyses per day using the atomic absorption method.

LEAD

Lead is found in nature primarily as the mineral galena (lead sulfide) but also as cerussite, anglesite, crocoisite, wulfenite, pyromorphite, matlockite and vanadinate. Since the inorganic salts of lead are relatively insoluble, the element most commonly enters a water supply via industrial, mine, and smelter discharges or through dissolution of old co-roded lead plumbing. The latter problem is much more common in areas where the water is "soft"; that is, it has a low hardness or mineral content.

Lead is an extremely toxic element which tends to exchange with calcium and accumulate in bone marrow. Lead toxicity may not appear until many years after the last exposure. Organic compounds of lead are many times more toxic than inorganic forms. The most common example is tetraethyl lead which is used as an "antiknock" additive in motor fuels. Organic lead exerts its toxic effect on the nervous system within a very short time causing mental confusion, delirium, nausea, hallucinations, insomnia, and convulsions. The maximum acceptable concentration of lead in domestic water is 0.05 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

When levels below the normal range of application are required, a notation must be included on the sample submission form so that the sample will be preconcentrated prior to analysis. One full 32 oz. bottle is required exclusively for the preconcentration process.

*NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 12 mg/l	.04 mg/l	± .02 mg/l

A portion of the sample is digested in a nitric-hydrochloric acid mixture and analysis is accomplished by atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 lead analyses may be completed per day.

LITHIUM

The element lithium is comparatively rare. It is concentrated in complex silicate minerals such as petalite and spodumene which are constituents of granite, nepheline syenite, pigmatites, and deposits of evaporate sediments. It is rarely found in surface waters and water supplies, but it has been detected in hot springs and highly mineralized brines where the concentration is usually less than 10 mg/l.

Lithium becomes toxic to animals and humans only if taken in very large amounts. When in sufficient quantity, it has the capacity for replacing sodium in body cells and thus upsetting intra-cellular metabolism. Cause of death is generally due to kidney failure although secondary effects on the nervous system are also observed. Small doses of lithium carbonate have been effectively used as an anti-depressant for treatment of psychiatric patients.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed containers are required for trace level determinations in domestic water and surface water samples. Glass bottles are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 2.0 mg/l	.02 mg/l	± .06 mg/l (at the 2.0 level)

Samples submitted for a lithium determination are digested in a nitric-hydrochloric acid mixture and analysis accomplished using atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 lithium analyses may be performed per day.

MAGNESIUM

Magnesium ranks eighth in the natural order of elemental abundance and is commonly found in the minerals magnesite, dolomite, olivine, serpentine, talc and asbestos. Its industrial applications include the manufacture of metal alloys, photographic flash bulbs, flares, and tracer bullets.

Magnesium is present in all natural waters and is generally associated with the presence of calcium. In natural fresh water systems the calcium concentration is approximately three to five times that of magnesium. If the reverse is found, an artificial source of magnesium is probable. In sea water, however, the concentration of magnesium exceeds that of calcium.

Magnesium is an essential element for the life functions of all plants and animals. It is closely associated with the metabolic activity of phosphorus where it is believed to act as an activator of phosphate enzymes. Ingestion of magnesium produces no adverse effects at levels normally encountered in domestic water supplies, but concentrations in excess of 125 mg/l exert a cathartic action on the gastro-intestinal tract.

Magnesium is a major contributor to water "hardness"; therefore limitations on the amount of magnesium in water supplies is of concern especially to industry (see Hardness).

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	GLASS OR PLASTIC	None * Required

*Non-routine industrial waste samples, or any other samples where high levels of heavy metals are suspected, should be sampled in acid washed plastic containers and preserved with 20 drops of nitric acid per bottle.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Titrimetric 2 - 100 mg/l	2 mg/l	± 1 mg/l
A.A.S. .004 - 1.0 mg/l	.004 mg/l	± .002 mg/l

Magnesium is normally determined by taking the difference between the calcium and the hardness levels and reporting this difference as mg/l of magnesium. Non-routine industrial waste samples, etc., are analyzed for magnesium using atomic absorption spectrophotometry.

Time of Analysis

Approximately 45 magnesium analyses may be completed per day using the titrimetric difference method and 50 per day using the atomic absorption method.

25/2/75

MANGANESE

Manganese is a common element in nature and found in numerous minerals which include pyrolucite, braunite, hauserite, manganese-spat, tephroite, knebelite and rhodomite. It is found at very low levels in natural waters, generally in the divalent (soluble) or quadravalent (suspended) state, but in the absence of dissolved oxygen the divalent state predominates. The permanganate anion, containing manganese in the heptavalent state, is not found in water unless it has been added artificially. High levels of manganese are usually the result of industrial discharges. Common industrial applications include the manufacture of metal alloys, dry cell batteries, paints, varnishes, inks, dyes, glass, ceramics, matches, fireworks, and fertilizer.

Manganese in trace quantities is essential for the proper nutrition of both animals and plants and is believed to be important in the metabolic oxidation-reduction processes of living cells. Manganese deficiency in animals is characterized by lack of growth, bowing and abnormal fragility of the bones, and degeneration of the reproductive organs. Manganese and its salts, ingested in very large quantities, are potent nerve toxins.

Although manganese is non-toxic at the levels commonly encountered in water supplies, it causes unpleasant tastes, stains laundry and plumbing fixtures, and encourages the growth of objectionable micro-organisms at treatment plants. The maximum acceptable concentration of manganese for domestic water supplies in Ontario is 0.05 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 4 mg/l	.04 mg/l	± .01 mg/l (At the 0.2 level)

Samples are digested in a nitric-sulfuric acid mixture and analysis is accomplished using atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 manganese analyses may be completed per day.

25/2/75

MERCURY

Mercury is a relatively rare element often found as the mineral cinnabar (mercuric sulphide). Mercury is seldom present in natural waters at levels exceeding 0.5 parts per billion. The solubility of metallic mercury in water is low (2 x 10^{-5} g/l), and the solubility of ionic mercury compounds depend upon the acutal conditions of the solubilizing water (i.e. acidity, presence of complexing anions, other organo-metallic complexes). As a result, the mercury content of surface water depends upon the accessibility of mercury, time of contact and conditions of the solubilizing media.

Mercury has many industrial applications which include (in order of consumption) electrical apparatus, chloralkali industry, paint, industrial control instruments, agriculture, dental applications, general laboratory use, paper and pulp production.

The greatest environmental hazard associated with mercury is its tendency to become concentrated in living organisms. Any form of mercury entering an aquatic system could be converted via bacterial activity to methyl mercury derivatives. These substances will then become concentrated along a food chain until they reach toxic levels and begin to endanger higher forms of life. In man, mercury exerts its toxic effects on the nervous system. Common symptoms include muscular tremors, speech impairment, lack of co-ordination and emotional disturbances.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
250 mls (9 ounces)	GLASS ONLY (NO FOIL LINED CAPS)	HNO_3 - $KMnO_4$ (See Below)

Preservation is accomplished by adding 1 ml of concentrated nitric acid (Baker analyzed only) per bottle and enough potassium permanganate solution (saturated) to maintain a slight purple color. Samples stored for over 3 days, even when preserved, may lose mercury. Immediate delivery to the laboratory is essential. Consultation with laboratory staff is advisable whenever mercury analyses are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 10 μg/l	.05 μg/l	± .03 μg/l (At the 0.2 Level) ± .14 μg/l (At the 8.8 Level)

Samples are first pretreated using a special acid digestion. Mercury vapor is then generated by the sequential addition of appropriate reducing agents and analysis accomplished via Flameless Atomic Absorption Spectrophotometry.

Time of Analysis

Approximately 20 mercury analyses may be completed per day.

MOLYBDENUM

Molybdenum is found in nature as the minerals molybdenite, wulfenite, and molybdenum ochre. Its industrial applications include the manufacture of steel alloys, glass, ceramics, pigments, lacquers, paints, electrical wiring, and fertilizer. It is also used as a catalyst in certain chemical processes. Its presence in natural waters is likely the result of industrial discharges.

In plants, molybdenum is believed to have an important influence on the ascorbic acid (vitamin C) equilibrium. It is essential to the nutrition of leguminous crops and all other nitrogen-fixing organisms. In animals, the function of molybdenum is not well understood but it appears to behave much like copper. It is known to be a constituent of certain flavoprotein enzymes which have essential metabolic functions.

Of all the industrial heavy metals, molybdenum is one of the least toxic. Isolated instances of molybdenum poisoning are generally associated with cattle grazing in pastures where the soil contains elevated levels of molybdenum (20-100 ppm). Normal soils contain between 3-5 ppm. This condition in cattle is commonly known as "teart" and is characterized by severe diarrhea, anaemia, and harsh discolored fur.

Molybdenum is rarely encountered in domestic water supplies and no limit has been specified for its maximum acceptable concentration.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* Note: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 10 mg/l	.04 mg/l	± .02 mg/l (At the 1.0 level)

Samples are pretreated by wet acid didgestion and analysis is accomplished via atomic absorption spectrophotometry using a nitrous oxide-acetylene flame.

Time of Analysis

Approximately 50 molybdenum analyses may be completed per day.

25/2/75

NICKEL

Nickel is more abundant in Ontario than anywhere else in the world. It is found primarily as the sulfide minerals pentlandite, chalcopyrite, pyrrhotite, and nickelblende as well as the arsenic minerals kupfernickel and nickelglance. Nickel has numerous industrial applications; the most important of which is the manufacture of high quality heat and corrosion resistant steel. Electroplating processes which utilize nickel are also widespread. Levels in natural waters are very low; therefore, if nickel is found, it is likely the result of an industrial discharge.

Nickel and its salts have generally proven to be non-toxic to man even at very high levels. Nickel sulfate and nickel bromide have even been used therapeutically as nervous sedatives for headache, neuralgia, and insomnia. However, nickel carbonyl is suspected of being carcinogenic although confirmatory evidence is not well established. No maximum acceptable concentration in domestic water supplies has been specified.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.07 - 7 mg/l	.07 mg/l	± .03 mg/l (at the 0.5 level)

Samples are digested with a nitric-sulfuric acid mixture and analysis accomplished using atomic absorption spectrophotometry. Nickel is one of the elements most suited to atomic absorption analysis in that it is essentially interference free.

Time of Analysis

Approximately 50 nickel analyses may be completed per day.

NITRATE NITROGEN-FILTERED

Nitrate is formed via the oxidation of nitrite by autotrophic nitrifying bacteria and represents the most highly oxidized form of nitrogen in the nitrogen cycle. It is generally found at trace levels in all surface waters but may become very high in ground water as a result of soil leaching. Nitrate provides an alternate source of oxygen when the dissolved oxygen has been depleted.

Nitrate results are of value in interpreting the effectiveness of the waste stabilization process at sewage treatment plants. Its abundance in treated water is an indication of how far treatment has progressed. Biochemical reduction of nitrate may frequently result in the production of nitrogen gas rather than ammonia (denitrification). This reaction is undesirable during the activated sludge process since the nitrogen gas tends to buoy the sludge and thereby inhibit digestion.

Nitrates are objectionable because their nutritive properties promote the excessive growth of algae and other aquatic plants. Although nitrates are considered non-toxic to adults, high levels in domestic water supplies contribute to a condition known as infant methemoglobinemia in which the oxygen carrying capacity of the blood is inhibited. The maximum acceptable level for domestic water supplies in Ontario is 10 mg/l of nitrate as nitrogen if the water is to be used for infant feeding.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Nitrate is unstable and is rapidly converted to other nitrogen compounds by bacterial action. Refrigeration is helpful but freezing is the preferred form of preservation.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 2.0 mg/l	.02 mg/l	± .01 mg/l

Samples are pretreated by filtration and passed over granular metallic cadmium where nitrate is reduced to nitrite. Subsequent analysis for nitrite is accomplished colorimetrically (see nitrite nitrogen). High levels of hexavalent chrome, trivalent chrome, copper, iron and various oxidizing agents are known to cause interference effects. Results are reported in mg/l of nitrogen.

Time of Analysis

Approximately 200 nitrate analyses may be completed in an 18 hour Auto Analyzer working period.

25/2/75

NITRILOTRIACETIC ACID (N.T.A.)

The trisodium salt of nitrilotriacetic acid is presently being used as a replacement for phosphates in detergent formulations. This has caused widespread concern since the consequences of N.T.A. discharges to the environment have not been well established.

At present there is no adequate evidence to support the premise that N.T.A. is an environmental hazard. N.T.A. has proven to be relatively non-toxic as well as biodegradable. Degradation products which include CO_2, H_2O, and inorganic nitrogen compounds are all safe naturally occurring substances. Of major concern is the possible interaction of N.T.A. with toxic trace metals. N.T.A. is a good chelating agent and may facilitate the transfer of toxic metals into biological systems over an extended period of time. Verification of this hypothesis may only be confirmed through long term studies.

Environmental monitoring of N.T.A. and research programs attempting to define possible environmental hazards associated with N.T.A. are likely to become increasingly more important in the near future.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
600 mls (One Full 20 Ounce Bottle)	GLASS ONLY (20 ounces)	FORMALDEHYDE (2 mls/20 oz. Bottle)

Submit one full 20 ounce glass bottle exclusively for N.T.A. analysis. Be sure to use caps with teflon liners.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 2.5 mg/l	.05 mg/l	Not Available

Samples are analyzed directly using a dropping mercury polarograph. Results are reported as the Acid.

Time of Analysis

Approximately 15 N.T.A. analyses may be completed per day by polarography.

NITRITE NITROGEN-FILTERED

Nitrite is present in natural waters as an intermediary in the oxidation of ammonia by autotrophic nitrifying bacteria or in the anaerobic reduction of nitrate. In either case, its presence is short lived with the concentration seldom exceeding 1.0 mg/l as nitrogen. Higher concentrations are indicative of an industrial effluent. Waters containing nitrite are in the midst of rapid chemical changes.

Nitrite results may be used in interpreting the effectiveness of the waste stabilization processes at sewage treatment plants, but these results must be interpreted with full allowance for extreme perishability. The usefulness of nitrite results are questionable since it is highly unlikely that the concentration at the time of analysis represents the concentration at the time of sampling.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Nitrite is unstable and is rapidly converted to other nitrogen compounds by bacterial action. Refrigeration is helpful but freezing is the preferred form of preservation. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.002 - 0.2 mg/l	.002 mg/l	± .001 mg/l

Samples are pretreated by filtration and analysis is accomplished colorimetrically via the diazotization reaction of nitrite with sulphanilic acid and 1-napthylamine. The colorimetry portion of the procedure is performed automatically using an Auto-Analyzer system. High levels of iron, hexavalent chrome, and copper are known to produce interference effects. Results are reported as mg/l of nitrogen.

Time of Analysis

Approximately 200 nitrite analyses may be completed in an 18 hour Auto Analyzer working period.

25/2/75

NITROGEN - TOTAL KJELDAHL

Total kjeldahl nitrogen is a measure of all the nitrogen in the trinegative state. It is primarily a measure of nitrogen present in the organic form, such as proteins, amines, urea, etc., but it also includes nitrogen present as free ammonia. It does not include nitrogen present as nitrite or nitrate. "Organic nitrogen" can be obtained by taking the difference between the free ammonia and the total kjeldahl nitrogen results. "Total nitrogen" may be obtained by taking the sum of the nitrite, nitrate, and total kjeldahl nitrogen results. Kjeldahl nitrogen is used as an indicator of sanitary water quality.

Kjeldahl nitrogen results are of great value in interpreting the effectiveness of the waste stabilization process at sewage treatment plants. Treatment follows a natural sequence of biochemical reactions in which nitrogen components are successively oxidized from organic nitrogen to ammonia, nitrite and finally nitrate. The relative abundance of each of these compounds in the treated water is an indication of how far treatment has progressed.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Kjeldahl nitrogen is slowly converted to other nitrogen compounds by bacterial activity. If representative results are expected, an analysis should be performed within two or three days after sampling. Samples must be refrigerated or frozen immediately after collection and delivered to the laboratory as soon as possible.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 2.0 mg/l	0.1 mg/l	± .05 mg/l

Samples are pre-treated by digestion with sulfuric acid and potassium persulfate. Analysis is accomplished colorimetrically by the alkaline phenol hypochlorite method adapted to an Auto Analyzer system. High levels of manganese, cobalt, iron, trivalent chrome and calcium are known to cause interferences. Kjeldahl nitrogen results are reported in mg/l of nitrogen.

Time of Analysis

Approximately 200 samples may be analyzed during an 18 hour Auto Analyzer working period.

ORTHOPHOSPHATES - FILTERED REACTIVE

The filtered reactive orthophosphate content of a sample is that fraction which passes through a filter and reacts during analysis to produce a positive colorimetric response. It is generally accepted that some organic and even particulate forms of phosphate can react similarly to dissolved orthophosphate under the analytical test conditions. The above terminology removes the implication that the test measures only orthophosphate forms which are uncombined and in solution.

Phosphorus is an essential element for all life forms. Artificial inputs of phosphorus via wastewater and land run-off play a significant role in promoting the overabundance of algae and aquatic plants which may impair water quality. However, the usefulness of filtered reactive orthophosphate results is questionable because of its extreme reactivity. Results must be interpreted with full allowance for perishability, both in situ and in the sample following collection.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Use only brand new containers when sampling for filtered reactive orthophosphate. Rewashed containers are likely to remain contaminated with a residual amount of phosphorus regardless of how thoroughly they are cleaned. Filtered reactive orthophosphate is readily converted to other phosphorus forms biologically; hence samples must be refrigerated or frozen immediately after collection and delivered to the laboratory as soon as possible.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.002 - 0.2 mg/l	.002 mg/l	± .001 mg/l

Samples are pretreated by filtration and analysis accomplished colorimetrically using an ammonium molybdate-stannous chloride technique which has been adapted to an Auto Analyzer system. High levels of silica, iron, trivalent chromium, hexavalent chromium, copper, zinc, and various oxidizing agents are known to cause interferences. Results are reported in mg/l of phosphorus.

Time of Analysis

Approximately 200 analyses may be completed during an 18 hour Auto Analyzer working period.

25/2/75

PESTICIDES (CHLORINATED HYDROCARBONS)

Chlorinated hydrocarbon type pesticides are widely used in agriculture, industry, wild life control and public health programs. Many of these materials are extremely stable and produce persistent residues in the environment. Biological accumulation of these residues in living cells are known to produce adverse effects on metabolic, enzymatic, neurological, and reproductive functions. Long term effects are not yet fully understood.

Samples submitted for the determination of CHLORINATED HYDROCARBONS will be analyzed for ∝BHC, βBHC, Lindane, Heptachlor, Aldrin, Dieldrin, Endrin, Heptachlor Epoxide, DDT, DDE, DDD, HCB and PCB's. The capability is available for analyzing many other classes of pesticides, herbicides and slimicides, but these are generally considered non-routine. Consultation with laboratory staff is recommended when other substances are suspected.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (32 ounces)	GLASS ONLY (See Below)	REFRIGERATE (Store in the Dark)

One clean, solvent rinsed, 32 ounce glass bottle clearly labelled "PESTICIDES AND PCB's ONLY" should be submitted exclusively for this type of analysis. Plastic bottles should not be used under any circumstances as they will adsorb chlorinated hydrocarbons. Fill the bottle only to the top of the label leaving an air space of about 150 mls. Bottle caps must be foil lined as any rubber or plastic caps may release extraneous organic substances to the sample. Avoid the use of plastic or lubricated sampling device.

Method

Range Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1.0 - 1000 ηg/l (Dependent on Compound Analyzed)	1.0 - 20 ηg/l (Dependent on Compound Analyzed)	± 5 - 10% (Dependent on Compound, Concentration and Interferences)

Pre-treatment includes concentration by solvent extraction, column chromatographic clean-up, and separation into chemical classes. Identification and quantitative analysis is accomplished by gas chromatography.

Time of Analysis

Samples are generally set up in groups of ten per day, but the routine systematic analysis is extremely complex and requires five days to complete. When PCB's are present, special separatory techniques must be employed and analysis will take even longer.

25/2/75

PETROLEUM HYDROCARBONS

Petroleum hydrocarbons include gasolines, aviation fuels, organic cleaners, thinners (e.g. Varsol), kerosenes, stove oils, home heating fuels, diesel fuels, lubricating oils, cutting oils and transformer oils. Many of these substances may impart objectionable tastes and odours to domestic water supplies at very low levels. They are also known to increase the oxygen depletion rate in receiving waters and will hinder oxygen exchange with the atmosphere by forming slicks.

Petroleum hydrocarbons are generally found as a complex mixture of organic compounds. Identifications are, therefore, generally reported as a class or type of material rather than as a specific substance. In some cases a semi-quantitative measurement can also be provided. Laboratory staff should be consulted whenever a water contaminant requires source identification.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (32 ounces)	GLASS ONLY	REFRIGERATE (See Below)

Open waters should be sampled at the surface as this is where petroleum hydrocarbons will collect. If closed plumbing systems are to be sampled, taps should not be opened for several hours prior to collection so that contaminants may build up. Tap sieves and toilet tanks are frequent areas where contaminants collect. Samples of the suspected contaminant source should be submitted with the contaminated water whenever possible.

One full 32 ounce bottle, clearly labelled "PETROLEUM HYDROCARBONS" should be submitted for this test exclusively. Bottle caps must be foil lined as any rubber or plastic caps may release extraneous organic compounds. Containers must be tightly capped and refrigerated to prevent the loss of volatile components. Petroleum hydrocarbons are susceptible to bacterial attack; therefore immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Not Available	Not Available	SEMI-QUANTITATIVE ONLY

An extraction is performed using an appropriate organic solvent and analysis is accomplished by gas chromatography.

Time of Analysis

Approximately 8 petroleum hydrocarbon determinations may be completed per day.

pH

pH is defined as the negative logarithim of the hydrogen ion activity, but in the case of natural water samples, the hydrogen ion ion activity closely approximates the hydrogen ion concentration in moles per liter. As the pH scale is logarithmic, a change of pH by one unit means a tenfold change in the hydrogen ion concentration. Rivers and lakes which have not been polluted by acid or alkaline wastes range in pH from about 5 (acid peat bogs) to 8.5 (chalk streams and marl lakes). In highly productive waters, photosynthetic activity can cause the overabundance of carbonate ion. This may also result in a natural pH close to 8.5.

Most surface waters are protected from fluctuations in pH by the natural buffering capability of the bicarbonate ion. Pollution by industrial wastes, however, can upset this equilibrium, and produce significant pH changes in the receiving water. A change in pH implies that changes in the alkalinity and acidity are also taking place. pH results are best interpreted in conjunction with the alkalinity and acidity.

pH is a highly perishable parameter because of its dependence on temperature, dissolved gas concentrations, and other chemical reactions. It should be measured in the field whenever possible. A laboratory pH measurement is not necessarily representative of the pH at the time of sampling.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
25 mls (1 ounce)	GLASS OR PLASTIC	* See below

*Bottles should be filled completely so that no air bubbles remain once the samples are capped. For sludges use widemouth glass bottles and fill only half way. Do not refrigerate. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0 - 14 pH Units	Not Available	± 0.1 pH Units

pH is commonly determined using a potentiometer that is sold specifically for the measurement of pH. A good quality instrument is essential for precise measurements.

Time of Analysis

Approximately 100 pH measurements are routinely performed per day.

25/2/75

PHENOLICS (REACTIVE)

Reactive phenolics are compounds having one or more hydroxy groups attached directly to an aromatic ring. This class of substance contains a large number of organic compounds but the term reactive phenolics is restricted to those compounds which can be distilled at atmospheric pressure and which respond to the selected colorimetric procedure. Since carbolic acid is used as the calibration standard, results are expressed as a carbolic acid equivalent in μg/l. These results represent the lowest possible values for the phenolic content.

The formation of chlorophenols during chlorination processes is believed responsible for a number of taste and odor problems in treated water supplies. In many cases these troublesome chlorinated phenols may not be detected by the available chemical methods. This implies that a taste and odor problem due to chlorophenols may be present even though the detected concentration of phenolic substances is low. It is, therefore, imperative that samples be collected before chlorination. If more specific analytical information regarding phenolic content is required, laboratory staff should be consulted.

The maximum accepted limit for reactive phenolics in the domestic water supplies of Ontario is 1 μg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
Full Special Container	Special Glass Container	Special Container with Preservative *

Since phenolic compounds are susceptible to bacterial attack they should be refrigerated and delivered to the laboratory immediately. * Samples are to be collected in special bottles which already contain the proper amount of preservative.

SAMPLES FROM TREATMENT PLANTS MUST BE COLLECTED BEFORE CHLORINATION.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
4 - AAP 2 - 50 μg/l	2 μg/l	± 0.5 μg/l
GIBBS 2 - 120 μg/l	2 μg/l	Not Available

Samples for phenol analysis are acidified with phosphoric acid and distilled at approximately 120° C. Analysis is accomplished colorimetrically using the automated 4-aminoantipyrine method or the manual Gibbs method. Any organic substance which is steam distillable is a potential interference.

Time of Analysis

Approximately 100 phenol analyses may be accomplished per day using the automated 4-aminoantipyrine method and 30 per day using the Gibbs method.

PHOSPHORUS - TOTAL

Phosphorus occurs in natural and waste waters in several different combinations, which include orthophosphates, pyrophosphates, metaphosphates, polyphosphates and organically bound phosphates. Phosphorus is an essential element for all life forms. As all of the above compounds may eventually be used in metabolic processes, determination of the total phosphorus concentration is more relevant than the measurement of individual phosphorus compounds.

Phosphates are used in the manufacture of fertilizers as well as detergents. Polyphosphates are used in some public water supplies and industrial boiler systems as scale and corrosion inhibitors. Artificial inputs of phosphorus via wastewater and land run-off play a significant role in promoting the over-abundance of algae and aquatic plants which impair water quality. Phosphorus results are used in assessing a water's potential for biological productivity as well as the efficiency of nutrient removal facilities at waste treatment plants.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE (See Below)

Contamination is a significant problem in determining total phosphorus concentrations. Re-washed bottles may contain residues of phosphorus, hence single-use glass containers or plastic are preferred. If using a re-washed container is unavoidable, it must be cleaned with 10% hydrochloric acid and thoroughly rinsed with distilled water prior to field use. Refrigeration or freezing is required only if other nutrient parameters are to be determined on the same sample.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.004 - 0.2 mg/l	.004 mg/l	± .002 mg/l

Samples are pre-treated by digestion with sulfuric acid and potassium persulfate and analysis accomplished colorimetrically using a phosphomolybdate technique which has been adapted to an Auto Analyzer system. High levels of silica, iron, trivalent chrome, hexavalent chrome, copper, zinc and various oxidizing agents are known to interfere. Results are reported as mg/l of phosphorus.

Time of Analysis

Approximately 200 samples may be analyzed during an 18 hour Auto Analyzer working period.

25/2/75

POTASSIUM

Potassium ranks seventh in the natural order of elemental abundance. It is highly soluble and present at trace levels in all natural surface water, but very seldom exceeds 20 mg/l. Brackish or saline ground water, however, may contain potassium in excess of 100 mg/l. Potassium is generally found in the presence of sodium and only in rare instances will it ever exceed the sodium concentration. When potassium is in greater abundance than sodium, an artificial source is likely.

Potassium is an essential nutrient for all life forms, especially plants, and is therefore a major component of commercial fertilizers. It is non-toxic and represents no known health hazard. No limits have been specified for the maximum acceptable concentration of potassium in domestic water supplies.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
40 mls (2 ounces)	PLASTIC (GLASS)	NONE REQUIRED

Under alkaline conditions, glass containers are attacked releasing potassium ions to the sample. Pyrex is more resistant than soft glass, but plastic containers are preferred. Glass containers are only adequate when neutral pH conditions are known to exist.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.4 - 6 mg/l	0.4 mg/l	± 0.2 mg/l

Samples are analyzed using an atomic absorption technique modified to an automated system.

Time of Analysis

Approximately 150 potassium analyses may be completed per day.

25/2/75

RESIN AND FATTY ACIDS

Mixtures of resin and fatty acids in water are generally associated with pulp mill effluents. They are produced in combination with other pulp waste components such as tannins and lignins so that waters containing these substances typically have severe taste, odor, and color problems.

Pulp mill effluents may contain mixtures of ten or more resin and fatty acids. Some examples include myristic, palmitic, stearic, oleic, pimaric, isopimaric, levopimaric, sandaracopimaric, abietic, and dehydroabietic acids. The more prevalent ones, such as pimaric, abietic and dehydroabietic acids, are detectable in receiving waters several hundred yards away from their point of origin.

Toxicity studies have confirmed that several of the resin acids are harmful to fish and other aquatic organisms at concentrations as low as 1 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (32 ounces)	GLASS ONLY	REFRIGERATE 2 Drops 10N NaOH

One full 32 ounce bottle clearly labelled "Resin Acids" should be submitted for this test exclusively. AN ANALYSIS CANNOT BE PERFORMED UNLESS THIS REQUIREMENT IS MET. Bottle caps must be foil-lined as rubber or plastic liners may release extraneous organic compounds into the sample. Loss of volatile acids is prevented by the addition of sodium hydroxide.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Variable	0.01 mg/l	Not Available

Samples are acidified and extracted with a suitable organic solvent. The extract is then treated with a drying agent and concentrated by evaporation. The concentrate is then injected directly into a gas chromatograph.

Time of Analysis

Approximately 5 resin and fatty acid determinations can be handled by one analyst per day. Because the analytical procedure is long and tedious, samplers are urged to use discretion when submitting samples.

SELENIUM

Selenium is naturally found in the form of metallic selenides, selenites, and selenates, and also as organic compounds derived from decayed plant material. Its common industrial applications include the manufacture of rectifiers, photoelectric cells, red colored glass, pigments, paints, dyes, and insecticides, as well as in the vulcanization of rubber as a supplement to sulfur.

Selenium is highly toxic, behaving in much the same manner as arsenic, and is believed to be a potentially carcinogenic agent. Selenium acts as an accumulative toxin in humans, causing rather vague symptoms such as gastric and nervous disturbances, dizziness, depression and fatigue. In cattle, selenium poisoning causes a condition commonly referred to as "blind staggers" or "alkali disease". Symptoms include impairment of vision, abdominal pain, partial paralysis, loss of hair, internal lesions and anaemia. Some researchers have presented evidence to indicate that trace quantities of selenium are important as catalytic agents in the respiratory enzyme systems of living cells, but this has not been confirmed.

Selenium is likely present in natural waters as the selenate anion ($SeO_4^{=}$) or as organic selenium compounds which have been discharged in industrial effluents. The maximum acceptable concentration of selenium for domestic water supplies in Ontario is 0.01 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	*ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

*NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.002 - 0.2 mg/l	.002 mg/l	Presently Not Available

Samples are analyzed fluorometrically using 2,3-diaminonaphthalene. Analysis of selenium is an exceptionally lengthy process.

Time of Analysis

Approximately 5 selenium analyses may be completed per day. Because the analytical procedure is long and tedious, samplers are urged to use discretion when submitting samples.

SETTLEABILITY

Settleability describes that portion of sample which will undergo gravitational separation (settling) during a 30 minute time interval. It is commonly performed as a routine control procedure at sewage treatment plants, although it is occasionally performed by the laboratory branch for historical purposes.

The determination of settleability is a simple procedure for evaluating the various stages of waste treatment. It is most valuable when performed at the treatment plant because visual qualities such as size, shape, and colour of the suspended particles as well as the optical properties of the supernatant are also observed during the analysis. Visual appearance may have more meaning in terms of treatment efficiency than the numerical value for settleability.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (one full 32 ounce bottle)	GLASS	NONE REQUIRED

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0-1000 ml/l	Not Available	Not Available (Empirical Method)

A known volume of well mixed sample is poured into an Imhoff Cone and allowed to settle for 30 minutes. The volume of settled material is then related to the total volume of sample and the results reported in ml/l of settleable material.

Time of Analysis

One analysis requires 45 minutes. If samples are analyzed in batches, six determinations can be completed in 90 minutes.

25/2/75

SILICATES - REACTIVE

The element silicon ranks second to oxygen in natural abundance and is present as silica or silicates in sand or quartz. In natural water silicates are generally found as monomers, polymeric chains and cyclic anions in both soluble and colloidal forms.

Silica and silicates are widely used in industry for the manufacture of glass, ceramics, abrasives and enamels and have been used in domestic water treatment as coagulants, corrosion inhibitors, and sequestering agents for iron. Their presence in boiler feed waters causes deposits of silica on steam-turbine blades, necessitating removal to concentrations as low as 0.1 mg/l in high pressure systems.

Silicates are essential to the growth of diatoms as well as many other aquatic organisms. No adverse physiological effects are known at concentrations generally found in natural or treated waters. Therefore, no maximum concentration has been specified for its presence in domestic water supplies.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	PLASTIC ONLY	NONE REQUIRED

Glass bottles should not be used since silicon is a major constituent of glass.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 5 mg/l	0.1 mg/l	±.05 mg/l

Samples are analyzed directly using the colorimetric molybdate method adapted to an Auto Analyzer system. Results are reported in mg/l of silicon. Iron, color, turbidity, tannins, sulfides, and phosphates in abundance are potential interferences.

Time of Analysis

Approximately 200 silicate analyses may be completed during an 18 hour Auto Analyzer working period.

SILVER

Silver is found in nature as the native metal, but its chief source is the mineral argentite. Besides being relatively rare, most of its compounds are insoluble; therefore it is highly unlikely that silver would appear in a domestic water supply unless introduced by artificial means. It is commonly used in the manufacture of silver utensils, jewellery, and solders as well as in the electroplating, photographic, and food processing industries.

Exposure to silver in industry is usually manifested as a condition referred to as argyria; common symptoms include a permanent blue-gray discoloration of the skin and eyes. Although excessive exposure to silver may result in kidney, liver, or spleen damage, no recognizable disturbance of health need accompany this condition.

The maximum acceptable concentration of silver in domestic water supplies is .05 mg/l. This limit is used to restrict the use of silver compounds as disinfectants and is indirectly based on public health considerations. Colloidal elemental silver in water is highly toxic and may result in blindness or death.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

Samples should be analyzed as soon as possible after collection. Silver compounds are easily adsorbed on the walls of containers.

* Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 4 mg/l	.04 mg/l	± .01 mg/l (At the 0.5 level)

Samples are pretreated using a wet acid digestion and analysis is accomplished by atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 silver analyses may be completed per day.

SLUDGE VOLUME INDEX

The sludge volume index (S.V.I.) is defined as one thousand times the ratio between "settleability" in ml/l and "suspended solids" in mg/l. It is a measure of how well a sample settles and compacts. When the suspended solids are high, settling characteristics become negligible and compaction determines the sludge volume index. An S.V.I. of less than 100 is indicative of a sludge with good compacting qualities.

The S.V.I. result is an empirical quantity with no assigned units. It is used by sewage treatment plant operators as an aid in selecting the rate of sludge return.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
See Settleability and Suspended Solids	See Settleability and Suspended Solids	See Settleability and Suspended Solids

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Not Available	Not Available	Not Available

The settleability of a sample in ml/l is divided by the suspended solids in mg/l and the result multiplied by 1000. The sludge volume index is exclusively a calculated parameter dependent only on the settleability and the suspended solids (see settleability and suspended solids).

Time of Analysis

The time required to determine the S.V.I. is dependent on the time required to perform the settleability and suspended solids determinations.

25/2/75

SODIUM

Sodium ranks sixth in the natural order of elemental abundance and is normally the principal ion in brackish or saline ground water. Sodium salts are used extensively in the manufacturing of chemical products as well as in commercial water softening devices which employ the sodium ion-exchange process. It is abundant in most industrial effluents. Waters that receive surface drainage from roads during the winter season can contain high levels of sodium as sodium chloride is used to control road ice.

Impairment of soil quality due to the presence of sodium is a major problem in agriculture. Soils high in sodium are generally characterized by low infiltration and permeability rates and are therefore unsuitable for farming.

Sodium is an important element for all life forms and is generally considered non-toxic. However, patients with high blood pressure are usually warned to avoid the consumption of water containing more than 50 mg/l of sodium. Waters, softened by the ion-exchange process employed in most domestic water softening equipment, generally contain sodium in excess of this amount; thus the private use of this process should be practised with discretion.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
40 mls (2 ounces)	PLASTIC	NONE REQUIRED

Under alkaline conditions, glass containers are attacked releasing sodium ions to the sample. Pyrex is more resistant than soft glass, but plastic containers are preferred. Glass containers should only be used for sampling when neutral pH conditions are known to exist.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.4 - 10 mg/l	0.4 mg/l	± .02 mg/l

Samples are analyzed via atomic absorption spectrophotometry.

Time of Analysis

Approximately 150 sodium analyses can be completed per day.

25/2/75

SOLIDS - DISSOLVED

Dissolved solids refers to the quantity of material that remains as a residue after the water is removed from a filtered portion of sample by evaporation. The test does not determine specific chemical substances but only a general class of substances which have a similar response under the same test conditions. "Total solids" may be found by taking the sum of the suspended and dissolved solids.

Dissolved solids may be determined in three different ways. Conductivity is the method of choice because it is the most precise and economical. Ontario lakes and rivers free of industrial wastes have a dissolved solids content equal to their conductivity times 0.65 ± 0.10. Some caution should be exercized in interpreting the results since the calculation methods based on either the conductivity or the summation of mineral components consider only the "ionic" dissolved solids.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS	REFRIGERATE

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
50 mg/l - Unlimited (Gravimetric)	50 mg/l (Gravimetric)	± 10 mg/l or ± 5% (whichever is greater) (Gravimetric)

Dissolved solids are determined:

Gravimetrically on all industrial waste samples as well as any other type of sample where the conductivity is greater than 450 micromhos/cm.

From the conductivity whenever the conductivity is less than 450 micromhos/cm.

From the sum of constituents by special request. Ca, Mg, Na, K, Cl, SO_4, NO_3, and alkalinity must all be determined on a particular sample in order to apply this technique.

NOTE: Total solids will be substituted for dissolved solids only when filtration becomes impractical e.g. raw sludges, digested sludges, mixed liquors, etc.

Time of Analysis

Two days are required to complete the gravimetric analysis. Samples are set up the first day and the weighing operation performed the second day. Approximately 75 samples may be set up per day.

25/2/75

SOLIDS - IGNITED

The ignited solids test determines both the quantity of material that remains as a residue and the quantity of material that is lost when either the total, suspended, or dissolved solids residue is ignited at 600°C for one hour. The test does not determine specific substances but only a general class of substances which have a similar response under the same test conditions.

The loss on ignition is due to oxidation of carbon and hydrogen, escape of water of hydration, volatilization of inorganic ammonium salts, decomposition of magnesium carbonate, and loss of any other materials which are volatile or decomposable below 600°C. Thus, the loss on ignition generally overestimates the organic content. The actual organic content is lower by the amount of water, inorganic salts, etc., released. In the case of clean natural waters, the loss on ignition is due almost entirely to non-carbonaceous material; therefore caution should be exercised in interpreting the results on such samples.

Ignited solids results are most useful in the characterization of sewage sludges where it is desirable to estimate organic composition. It is one of the major tests used in assessing the efficiency of sludge digestion.

Any inaccuracies associated with the total, suspended, and dissolved solids determinations are also an integral part of the ignited solids result. Additional errors resulting from mechanical losses due to decrepitation are also a possibility.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
See Dissolved and Suspended Solids	GLASS	REFRIGERATE

Method

Range Undiluted Sample	Detection Limit	Precision (Standard Deviation)
100 mg/l-Unlimited	100 mg/l	± 10%

Analysis is accomplished gravimetrically by taking the total, suspended, or dissolved solids residue and igniting it at 600°C for one hour.

Time of Analysis

Approximately 75 ignited solids determinations may be completed per day.

SOLIDS - SUSPENDED

Suspended solids refers to the quantity of material that may be removed from a water sample by filtration. The test does not determine specific chemical substances but only a general class of substances which have a similar response under the same test conditions.

The measurement of suspended solids is often improperly used in assessing water clarity. Clarity is a function of a water's optical properties and rarely relates to the quantity of suspended material present. Turbidity is a much better measurement of water clarity than suspended solids.

Suspended solids data is useful in evaluating the strength of domestic wastewater and in assessing the efficiency of waste treatment procedures. It is important in calculating loadings to aeration tanks, digesters, lagoons, and sedimentation tanks.

Acquiring a representative aliquot for analysis is the major source of analytical variability in the suspended solids measurement. Results on samples which contain large particles or more than 0.2% suspended material by weight are questionable because of rapid settling. Since there is considerable analytical variability in the results when the suspended solids concentration is less than 10 mg/l, samplers are urged to substitute a turbidity measurement as often as possible.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
200 mls (7 ounces)	GLASS	REFRIGERATE (Do Not Freeze)

A non-routine modification has been developed to extend the detection limit down to 0.2 mg/l. Low level suspended solids determinations are useful in special studies which involve loadings due to land drainage. Laboratory staff should be consulted if low level measurements are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
4 - Unlimited	4 mg/l	± 2 mg/l or ± 5% (whichever is greater)

Analysis is accomplished by filtering a known volume of sample through a preweighed filter paper (Reeve Angel 934 AH). The filter is then dried to constant weight at 103^o - 106^oC and results reported as mg/l of suspended solids.

Time of Analysis

Two days are required to complete the analysis. Samples are filtered the first day and the weighing operation performed the second day. Approximately 125 samples may be set up per day.

25/2/75

SOLVENT EXTRACTABLES

The solvent extractable test measures the total quantity of substances present in a water sample that is readily soluble in an appropriate organic solvent. Such substances include fatty acids, petroleum products, oils and greases, resins, etc. They are generally found in effluents of oil refineries, meat packing plants, slaughter houses, dairies, canneries, and a variety of other industries.

Solvent soluble materials greatly increase the oxygen depletion rate in receiving waters and will hinder oxygen exchange with the atmosphere by forming slicks. Their presence is exceptionally troublesome in sewage treatment processes where they are resistant to anaerobic digestion and accumulate within the digesters as scums.

The test does not measure the total organic concentration and if an identification is performed on the extracted material, it will not necessarily be representative of what was originally in the sample. Basic and volatile compounds, for example, are not included in the determination. If anything other than a rough guide to the organic content is required, laboratory staff must be consulted.

Clear instructions must be given as to whether solvent extractables are required on the aqueous layer, the organic (oil) layer, or the total sample. Twigs, leaves, etc., are to be excluded as much as possible.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (32 ounces)	GLASS	REFRIGERATE

One full 32 ounce bottle, clearly labelled "SOLVENT EXTRACTABLES ONLY", must be submitted for this test exclusively. Bottle caps must be foil lined as any rubber or plastic caps may release extraneous organic compounds to the sample. Do not use any chemical preservative. Solvent extractable substances are susceptible to bacterial attack; therefore immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
2 - 100 mg/l (may be extended where applicable)	2 mg/l	± 1 mg/l

An aliquot of the homogenized sample is acidified and extracted with a carbon tetrachloride/ethyl ether mixture. The solvent is then evaporated until the residue comes to a constant weight. The reported result is the residue weight in mg/l.

Time of Analysis

Approximately 10 solvent extractable determinations may be completed per day.

25/2/75

STRONTIUM

Strontium occurs in nature as the minerals celestite, strontianite, and apatite. Natural compounds of strontium are relatively insoluble; therefore, its presence in domestic water supplies in generally very low. Industrial applications of strontium and its compounds include the manufacture of metal alloys, storage batteries, paints, rubber, cathode ray tubes, tracer bullets and flares; its use, however, is not widespread.

The chemical behavior of strontium closely resembles that of calcium with a tendency to become concentrated in the human skeletal system. Strontium 90, the radioactive forms which results from nuclear fallout, is included in the routine monitoring of radioactive components in Ontario's waters conducted by the Ministry of Health. No chemical limits have been specified as to the maximum acceptable concentration of strontium in domestic water supplies.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.01 - 1.0 mg/l	.01 mg/l	Presently Not Available

Samples are prepared by a wet acid digestion and analysis accomplished using atomic absorption spectrophotometry. Interference by silica, zinc, aluminum,titanium, phosphate, and sulfate are suppressed by the use of lanthanum and a nitrous oxide-acetylene flame. Potassium nitrate is added to suppress ionization.

Time of Analysis

Approximately 50 strontium analyses may be completed per day.

25/2/75

SULFATE

Sulfate is an ionic component of all natural waters and is widely distributed in nature. It normally varies between 10 and 80 mg/l in natural waters, but may increase to several thousand mg/l when industrial discharges are involved. Rainfall may contain considerable amounts of sulfate if local industrial processes are emitting sulfur dioxide and sulfur trioxide to the atmosphere. Sulfate tends to be exceptionally abundant in mine drainage wastes where it is produced via pyrite oxidation.

Waters high in sulfate tend to form hard scales in boilers, heat exchangers, and plumbing in general. Under anoxic conditions sulfates serve as an oxygen source for bacteria which convert it to hydrogen sulfide gas; the latter is recognizable by its characteristic odour of rotten eggs. Sulfate is also believed to be responsible for "crown" corrosion in concrete sewer pipes.

The maximum sulfate concentration permissible for domestic supplies in Ontario is 250 mg/l. Concentrations above this level are non-toxic, but tend to exert a cathartic effect on the gastro-intestinal tract.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	None Required

A non-routine modification has been developed to extend the detection limit down to 0.2 mg/l. Applications include rain water analysis and special studies. Laboratory staff should be consulted if low level measurements are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
2 - 50 mg/l	2 mg/l	±1 mg/l

Sulfates are determined spectrophotometrically on an Auto Analyzer system using methyl thymol blue as the colorimetric reagent. No manual pretreatment steps are necessary. Interference effects occur when sulfide, sulfite, or yellow coloured substances are present in the sample.

Time of Analysis

Approximately 100 sulfate determinations may be completed per day.

SULFIDE

Sulfide is formed by bacterial reduction of sulfate and organic sulfur compounds under anaerobic conditions. It is, therefore, commonly found in domestic wastewater, industrial wastewater, sludges, hypolimnions of stratified lakes and any other aquatic systems where anaerobic conditions prevail. Its characteristic odor of "rotten eggs" is highly objectionable.

Sulfide is an important parameter in waste treatment monitoring. Oxidation of sulfide to sulfuric acid in concrete sewer pipes leads to "crown corrosion". Soluble sulfides in excess of 200 mg/l are toxic to bacteria and will inhibit sludge digestion.

Samples containing sulfides are unstable and results must be interpreted with caution.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (One Full 32 ounce Bottle)	GLASS OR PLASTIC	$Zn(C_2H_3O_2)_2-Na_2CO_3$ REFRIGERATE (See Below)

Samples must be collected with a minimum amount of agitation as sulfides are highly volatile and susceptible to oxidation by dissolved oxygen. Fill the container completely so that no air bubbles remain after the sample is capped. Immediate delivery to the laboratory is essential.

Preservation is accomplished by adding 2 mls of 2N zinc acetate solution to the sample followed by the dropwise addition of a 5% sodium carbonate solution until precipitation is complete. Consultation with laboratory staff is recommended when sulfide analyses are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Methylene blue 0.2 - 2 mg/l	0.2 mg/l	± 0.1 mg/l
Molybdate .02 - 1000 mg/l	.02 mg/l	± .02 mg/l (At the 0.4 Level)

Samples are acidified and analysis accomplished colorimetrically using the ammonium molybdate or methylene blue methods. The semi-quantitative lead acetate method is only used to obtain a rough estimate of the sulfide concentration. The ammonium molybdate method is the most precise and is essentially interference free. It is the method of choice whenever the best data is required. Caution must be exercised in interpreting the data as organic sulfur compounds may release sulfide under the test conditions. Levels lower than those indicated above will be provided only on special request. Sulfide results are reported in mg/l as H_2S.

Time of Analysis

Approximately 15 sulfide analyses may be completed per day using the ammonium molybdate method.

TANNINS AND LIGNINS

Tannins and lignins are members of a large group of hydroxylated aromatic compounds. They are natural components of plant material and are found in surface waters as a result of normal biochemical degradation processes, or as a result of industrial discharges. They are commonly found in the effluents of the paper and tanning industries. Tannins are also applied internally to boilers in order to facilitate the handling of calcium sludge deposits and to prevent the formation of a hard scale. Tannins and lignins are undesirable because they impart objectionable tastes and colours to domestic water supplies even at very low levels.

At present no separations or individual determinations of tannins and lignins are performed. Results are standardized and reported as mg/l of tannic acid. To convert this result to a lignin number, the tannic acid value should be multiplied by 2.5.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
200 mls (7 ounces)	GLASS	REFRIGERATE ONLY

Since tannins and lignins are subject to normal biochemical oxidation, samples should be refrigerated to retard bacterial activity. No chemical preservative should be used as this may interfere with the analysis. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1.0 - 10 mg/l	1.0 mg/l	± 1 mg/l

Tannins and lignins are determined colorimetrically by direct treatment with tungstophosphoric and molybdophosphoric acids (Tyrosine reagent). As other reducing agents produce the same color, their presence may cause an over-estimation of the actual tannin and lignin content.

Time of Analysis

Approximately 40 tannin and lignin analyses may be completed in one day.

25/2/75

TITANIUM

Titanium is found in nature as the minerals rutile, ilmenite, and sphene. It ranks eighth in the natural abundance of elements and is readily found in most soils, varying between 0.5 and 10%. The high tensile strength and corrosion resistant properties of titanium metal are valuable in the manufacture of special steel alloys which are used for structural purposes in aircraft frames and engines. Titanium metal is also used in the manufacture of electrodes, lamp filaments, and x-ray tubes. Oxides of titanium are used as a white pigment in the paint, glass, and ceramics industries. Titanium and its salts are generally extremely inert and insoluble; the notable exception is titanium tetrachloride, which is highly corrosive.

There is no known toxicity to humans, animals, or plants. Surgical appliances are generally made of titanium and various titanium derivatives have been used in the treatment of skin disorders. No limits have been specified for the maximum acceptable concentration of titanium in domestic water supplies.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 1 mg/l	.04 mg/l	± .02 mg/l

Samples are digested using a mixture of oxalic, sulfuric and nitric acid. Final analysis is accomplished colorimetrically using Tiron (Disodium-1, 2-Dihydroxybenzene 3, 5-Disulfonate). This method is highly specific for titanium and interference effects are essentially negligible.

Time of Analysis

Approximately 20 titanium analyses may be completed per day.

25/2/75

TURBIDITY

The turbidity is a measure of the optical properties of a sample which causes light to be scattered rather than transmitted in a straight line. Historically, turbidity was measured using a Jackson Candle turbidimeter, but the insensitivity of this instrument led to the development of secondary techniques which can measure the much lower turbidities commonly encountered in modern water treatment processes. The instrument currently employed at the laboratory is fundamentally different in optics and cannot be validly calibrated against the Jackson Candle turbidimeter.

Clarity is one of the main criteria which the public uses in judging water quality, either for drinking or for recreational use. This makes the measurement of turbidity a much more valuable gauge of water quality than the suspended solids test, which measures only the weight of particles present in suspension and has little direct bearing on the appearance of the water. It is recommended that field staff make greater use of turbidity in place of suspended solids measurements.

Care must be used in interpreting turbidity results since these are defined by the instrument, the standards and the optical phenomena being measured. Standards other than Formazin are exceedingly difficult to reproduce as their optical properties depend on the size, shape, and refractive index of the component particles in suspension.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	KEEP IN DARKNESS

Samples should be stored in darkness and delivered to the laboratory within 24 hours.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 1000 FTU	.05 FTU	± 2%

Light scattered by the sample at 90^o ± 30^o is measured in a nephelometer calibrated with Formazin standards. Results are reported in Formazin Turbidity Units (FTU). Rapidly settling particles, gross debris, or dissolved colored substances may invalidate the results.

Time of Analysis

Approximately 150 turbidity determinations may be performed per day.

25/2/75

URANIUM

Uranium is found in nature as the mineral carnotite as well as in igneous type rocks. It is well known for its radioactive properties since its major industrial application is the manufacture of nuclear fuel. Natural uranium, however, is present as the isotope U^{238}, which is not strongly radioactive.

In natural waters uranium is hexavalent and commonly present as the uranyl ion UO_2^{++}. Uranyl salts are very soluble and produce an objectionable taste and colour when they exceed a concentration of 10 mg/l as uranium. At considerably higher levels, ingestion of water containing uranyl ions may result in possible kidney damage. Limits on the maximum concentration of uranium in domestic water supplies, when specified, are generally based on chemical properties of the uranyl ion rather than on radioactivity.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.01 - 1.0 mg/l	.01 mg/l	Presently Not Available

Samples are pretreated with granular zinc to reduce all uranium to the proper valency. Analysis is then accomplished colorimetrically using ARSENAZO III.

Time of Analysis

Approximately 10 uranium analyses may be completed per day.

25/2/75

VANADIUM

Vanadium occurs in nature as the minerals vanadinate, patronite, mottramite, and carnotite, and is generally found in the presence of selenium. It is most valuable in the steel industry where it is known to increase the general toughness and tensile strength of certain alloys, but it is also used in the manufacture of dyes, paints, inks and ceramics. The presence of vanadium in natural waters is likely the result of industrial discharges.

The usefulness of vanadium in animal and plant metabolism has not been convincingly demonstrated and its behaviour in biological systems is not well understood. Some experimental evidence suggests that the presence of vanadium in trace quantities may be beneficial in the prevention of heart disease.

Several compounds of vanadium are known to be toxic in high concentration. Exposure may produce nausea, diarrhea, abdominal pain, nervous trembling of the hands, and greenish-black discoloration of the tongue. No limits have been specified for the maximum concentration of vanadium in domestic water supplies because the element is rarely encountered.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	*ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 100 mg/l	0.1 mg/l	±0.05 mg/l (At the 1.0 mg/l level)

Samples are pre-treated using a wet acid digestion and analyzed by atomic absorption spectrophotometry. Interferences are suppressed by the addition of aluminum chloride to a concentration of 1000 ppm.

Time of Analysis

Approximately 50 vanadium analyses may be completed per day.

25/2/75

VINYL CHLORIDE (MONOMERIC)

Monomeric vinyl chloride is a colorless, odorless gas which is slightly soluble in water at normal temperatures. It is widely used in industry for the manufacture of polyvinyl chloride and other related plastics. It also has some application as an extraction solvent for heat sensitive substances and as a refrigerant.

Vinyl chloride is not found in natural waters. Its presence could only originate through industrial sources. Furthermore, since it is a gas, it would not linger in an aqueous environment for any extended period of time. Sampling should be discriminately conducted only in areas where vinyl chloride is produced or utilized with full regard to its instability.

The significance of dissolved vinyl chloride in water is not totally understood. Some studies have indicated carcinogenic behaviour.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
10 ml	* SPECIAL GLASS BOTTLE	STORE IN THE DARK

* Sampling for vinyl chloride requires the use of a 15 ml glass "HYPOVIAL" which is filled with exactly 10 ml of sample and immediately stoppered with a rubber septum. This septum is then hermetically sealed with an aluminum ring using a crimping device. All the appropriate sampling equipment may be obtained from the Toronto Laboratory.

PLEASE CONTACT THE LABORATORY BEFORE ANY SAMPLING EFFORTS ARE INITIATED.

Method

Range on Undiluted Samples	Detection Limit	Precision (Standard Deviation)
Not Available	5 mg/l	± 2 mg/l

The "hypovial" containing the sample is heated to ensure that all the vinyl chloride is in the gaseous state. A sample of the gaseous substances in the container headspace is then taken by inserting a syringe through the rubber septum. Analysis is accomplished by direct injection into a gas chromatograph.

Time of Analysis

Approximately 15 vinyl chloride (monomeric) determinations may be completed per day.

25/2/75

VOLATILE ACIDS

Low molecular weight organic acids which are readily distilled from aqueous solution at low temperatures are commonly called volatile acids. They include acetic, propanoic, and butanoic acids as well as small amounts of valeric, isovaleric, and caproic acids. These volatile acids are formed as intermediates during the anaerobic degradation of carbohydrates, proteins and fats in sludge treatment processes. An excess accumulation of these acids can have a deleterious effect upon anaerobic digestion. In routine operation of an anaerobic waste treatment system, the volatile acid concentration is primarily used as the determining and controlling factor for maintaining a satisfactory balance between the saprophytic and methane producing bacteria which are largely responsible for the efficiency of anaerobic digestion.

Volatile acids are found in natural waters when anoxic conditions are prevalent, but they are extremely unstable and would not likely be found in domestic water supplies.

Results are reported as mg/l of acetic acid.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
25 mls (1 ounce)	GLASS	REFRIGERATE

Sludges should be collected in wide mouth glass jars and not filled more than half way. As volatile acids are extremely unstable, they should be maintained at 4°C and delivered to the laboratory immediately.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
50 - 2500 mg/l	50 mg/l	± 25 mg/l

Volatile acids are separated by means of a column chromatographic technique using a chloroform-butanol elutant. The eluate is then titrated with standard alcoholic sodium hydroxide to the phenophthalein endpoint. This procedure is capable of eluting higher molecular weight organic acids as well as some synthetic detergents; however, the concentration of these substances is generally negligible in sludges.

Time of Analysis

Approximately 20 volatile acid determinations may be completed per day.

ZINC

Zinc is commonly found in nature as zinc sulfide in the mineral sphalerite and as zinc carbonate in the mineral calamine. It is widely used in the manufacture of metal alloys such as brass, batteries, dyestuffs, paints and ointments, as well as in electroplating. Zinc most commonly enters a water supply via the deterioration of galvanized iron, the dezincification of brass, and direct industrial discharges.

In plants, zinc is an essential nutrient for normal growth. Plants growing in a zinc deficient soil are severely stunted. In animals, zinc is an important constituent of a number of enzymes, notably carbonic anhydrase which is vital for normal respiration. Zinc and its compounds are relatively non-toxic when taken orally. Even at high concentrations, nausea and diarrhea are the only adverse effects likely to be encountered. The limiting factors which determine the acceptable maximum concentration in a water supply are taste and appearance. Zinc, in excess of 5 mg/l, imparts a bitter astringent taste, a milky appearance in alkaline waters, and may cause a greasy film when the water is boiled. The maximum acceptable limit for domestic water supplies in Ontario is therefore 5 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	* ACID WASHED PLASTIC (GLASS)	HNO_3 (20 Drops/Bottle)

* NOTE: Special acid washed plastic containers are required for trace level determinations in domestic water and surface water samples. Glass containers are required for domestic waste and industrial waste samples.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 5 mg/l	.05 mg/l	± .02 mg/l (at the 0.4 level)

Samples are digested with a nitric-sulfuric acid mixture and analysis is accomplished using atomic absorption spectrophotometry. Very high (0.5%) levels of calcium, sodium, or potassium can interfere with the zinc analysis. If the presence of such species is suspected, the laboratory should be informed.

Time of Analysis

Approximately 50 zinc analyses may be completed per day.

BIBLIOGRAPHY

1) Standard Methods for the Examination of Water and Wastewater, 13th Edition, APHA (1971).

2) Klein, L., Chemical Aspects of River Pollution, Butterworth (1962).

3) Sawyer and McCarty, Chemistry for Sanitary Engineers, 2nd edition, McGraw-Hill (1967).

4) Browning, E., Toxicity of Industrial Metals, Butterworth (1961).

5) Report of the Committee on Water Quality Criteria, Federal Water Pollution Control Administration, U.S. Dept. of the Interior (1968).

6) Crosby, Dennis, and Stevens. An Evaluation of Some Methods for the Determination of Fluoride in Potable Waters and other Aqueous Solutions. Analyst 93, 643 (1968).

7) Rigler, F.H., The Phosphorus Fractions and the Turnover Time of Inorganic Phosphorus in Different Types of Lakes. Limn. and Ocean. 9, 511 (1964).

8) Fitzgerald, G.P. and Faust, S.L., Effect of Water-Sample Preservation Methods on the release of Phosphorus from Algae, Limn. and Ocean. 12, 332 (1967).

9) Methods for Chemical Analysis of Water and Wastes, U.S. Dept. of the Interior, FWPCA (1971).

10) Traversy, W.J., Methods for Chemical Analysis of Waters and Wastewaters, Canada Dept. of Fisheries and Forestry, Water Quality Division, Inland Waters Branch (1971).

11) Kopp, J.F. and Krones, R.C. Trace Metals in Waters of the United States, U.S.Dept. of the Interior, FWPCA, Division of Pollution Surveillance (1967).

12) Hem, J.D., Study and Interpretation of the Chemical Characteristics of Natural Water, U.S. Dept. of the Interior, Geological Survey (1965).

13) Parker, C.R., Water Analysis by Atomic Absorption, Varian Techtron Pty. Ltd. (1972).

14) Drinking Water Objectives, OWRC, (1967).

15) Guidelines and Criteria for Water Quality Management in Ontario, Ontario Ministry of the Environment (1974).

16) Unesco, Monographs on oceanographic methodology 1.) Determination of photosynthetic pigments in sea water, p.69 (1966).

APPENDIX I - Non-routine services provided by the Organic Trace Contaminants Section (O.T.C.S.).

Because of wide variations in composition, occurrence and reactions of organic substances, it is impossible to issue general guidelines on sampling techniques. Users of O.T.C.S. services are requested to contact either the respective supervisors or head technicians regarding sampling procedures, types of containers, and the number and volume of samples required. Consultation with the analyst is required before any samples are submitted. Please remember that a brief description of the general problem and specific information about the sample (i.e. sampling site, time, consistency, exposure to atmospheric conditions, etc.) are invaluable to the analyst in assessing the situation.

The tests listed below are available upon special request.

I Chromatography Section

Printing Solvents	- Ethyl Acetate
	- Toluene
Detergent Additives	- Citric Acid
Plastic Monomers	- Methyl Acrylate
	- Styrene
General	- Phthalic Acid
	- Maleic Acid
	- Benzaldehyde

II Organic Micropollutants and Pesticides Section

Organochlorine Pesticides	- Lindane
	- Heptachlor
	- Aldrin
	- Dieldrin
	- Endrin
	- Heptachlor Epoxide
	- pp' DDE
	- pp' DDT
	- pp' DDD
	- op' DDT
	- HCB
	- Chlordane
	- Toxaphen
	- Thiodan
	- Methoxychlor
Polychlorinated Biphenyls	
Organophosphate Pesticides	- Dichlorvos
	- Thimet
	- Mevinphos
	- Diazinon
	- Ronnel
	- Parathion
	- Malathion
	- Ethion
	- Methyl Trithion
	- Dursran

Triazine Herbicides	- Propazine - Atrazine - Prometryne - Simazine - Sencor - Bladex - De-Ethylated Atrazine - Cynazine - Ametryne
Chlorophenoxy and Chlorobenzoic Herbicides	- 2,4 D - 2,4,5 - T - 2,4 - DB - Silvex - MCPA - MCPP - Dicamba - Hydroxy-Dicamba

III Spectroscopy Section

Identification of Heavy Oils
Identification of Synthetic Coating Materials
Fibres
Phenolic Substances in Industrial Wastes

IV Mass Spectrometry Section

Identification and confirmation of organic and organo-metallic compounds.

APPENDIX II - Services of the Sediment and Soils Laboratory

Sediments and soils include sediment, soil, vegetation and other related solid and semi-solid substances. Many of the tests are the same as those for water and waste water samples. The primary difference is in the preparation prior to analysis and the specialized procedures which are required when accounting for interference effects. As the majority of analytical procedures are long and tedious, samplers are urged to use discretion when submitting samples.

Sample Handling and Preservation

Wide mouth glass jars are preferred for soil and sediment samples. "Whirl Seal" self-sealing plastic bags are acceptable for vegetation samples. Since each sample is analyzed in duplicate, it is important that a sufficient quantity of sample be submitted for analysis. Generally a full 4 ounce jar will contain enough sample for all chemical tests. A full 32 ounce jar is required for physical tests. All components may undergo some changes during storage. Tests for "total" analysis involve a digestion step so that these changes are not considered important. Tests for perishable parameters require that the sample be dried or placed into cold storage ($4^{O}C$).

Submitting Samples

A detailed description of known or suspected constituents should be included with every submission if there is an unusual or potentially hazardous one. Detailed sample descriptions are most valuable in assessing interference effects and how to account for them. If a series of samples are submitted from the same general locality, some indication as to how they relate to one another is very useful (e.g. a map of the various sampling points). This type of information assists the analyst in detecting anomalous results. The exact analyses must be listed on the submission forms. If there is some doubt as to what analyses to request, a brief description of the problem or purpose of sampling will enable laboratory staff to choose the appropriate tests. Delays in sample processing are most frequently due to uncertainties on the submission forms. Samplers should always include their telephone numbers on the submission forms so that any difficulties could be promptly resolved. Consultation with laboratory staff is recommended prior to any major sampling effort.

The following is a list of tests routinely conducted by the Sediments and Bio-Materials Laboratory. Special tests must be arranged with laboratory staff prior to submission of samples.

Physical Parameters for soil and sediments

- Particle size 1) Sieve technique
- 2) Hydrometer technique
- Plasticity
- Permeability
- Moisture Content

Chemical Parameters

- Loss on Ignition (ignited solids)
- pH
- Biochemical Oxygen Demand (BOD)
- Chemical Oxygen Demand (COD)
- Nitrogen - Total
- Phosphorus - Total
- Petroleum Hydrocarbons *
- Pesticides * (See Appendix I)
- Phenolics *
- Chloride *
- Fluoride *
- Sulfate *
- Sulfide
- Cyanide
- Sodium
- Potassium
- Calcium
- Magnesium
- Heavy Metals*
  - Aluminum
  - Arsenic
  - Cadmium
  - Chromium
  - Cobalt
  - Iron
  - Lead
  - Manganese
  - Mercury
  - Molybdenum
  - Nickel
  - Titanium
  - Vanadium
  - Zinc

* Parameters commonly reported in terms of an "extractable" concentration rather than a "total" concentration. On special request, heavy metals may also be analyzed as an "extractable" concentration.

TD
380
O57
1975